Evaluation of polychlorinated biphenyls, polychlorinated dibenzo-p-dioxins and dibenzofurans in street dust and wipe samples

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Abstract

Within this thesis rapid approaches to screening for the presence of polychlorinated dibenzo-p-dioxins, dibenzofurans (PCDD/PCDFs) and polychlorinated biphenyls (PCBs) in street dust and wipe samples were validated and applied in environmental monitoring or as part of governmental inspection programs. Generally, instrumental analysis was based on gas chromatography coupled to high resolution mass spectrometry (GC/HRMS) and quantification was based on isotope dilution analysis.

Street dust samples were collected using a natural bristle brush and stainless steel scoops. Mass recovery of fine-particle sea sand (a dust surrogate) on asphalt and concrete surfaces was used as a criterion for the effectiveness of sampling. Better mass recoveries of the dust surrogate were achieved on concrete than on asphalt surfaces. A wipe sampling method based on solvent wetted cotton wipes was evaluated for the investigation of transfer efficiencies during the sampling of PCBs and PCDD/PCDFs in particulate films (PFs) and oily liquid films (OFs). For PFs sufficient transfer efficiencies of low concentrated PCB and PCDD/PCDF congeners in 1g/m^2 spiking surrogate were achieved after the first wipe using n-hexane as wetting solvent. Transfer efficiencies for oily liquid films (OFs) were highest in the first wipe if n-hexane and n-heptane were used as compared to toluene. The spiking experiments of OFs showed a log-linear correlation between the number of wiping procedures and transfer efficiency which indicates that transfer efficiencies were constant in subsequent wipes.

For the extraction of PCBs and PCDD/PCDFs from street dust samples an extraction temperature optimization for a pressurized liquid extraction (PLE) method was developed and compared with Soxhlet extraction for the analysis of PCBs in real street dust samples. Toluene was used as the extraction solvent in both cases. During this study, a combination of toluene and PLE achieved better extraction efficiencies than Soxhlet extraction. Finally, the performance of the PLE method was evaluated by analysing NIST (National Institute for Standards and Technology) Standard Reference Material 1649a for PCB and PCDD/PCDF concentrations. This demonstrated that the accuracy of the PLE method for the determination of both substance classes was satisfactory. Additionally, for wipe sample extraction it could be successfully demonstrated that PLE is a suitable tool. The feasibility of the wipe sampling method was demonstrated on various impervious surfaces of different origin, and concentration levels of PCBs (PCB6: 0.0062 (exterior window surface of a resident house) – 1408 µg/m^2 (working area of transformer recycling); dl-PCBs: 0.00072 (exterior window

surface of a resident house) – 34 ng/m^2 (working area of transformer recycling)) and PCDD/PCDFs (0.00045 (exterior window surface of a resident house) – 1614 ng/m^2 (accidental heavy fires)) in wipe samples were discussed.

Street dust samples were taken from rural, urban, industrial and industrially influenced urban areas. PCB6 concentrations ranged from 5090±2200 µg/kg (average±standard error of mean) in dusts from industrial premises to 29±8.7 µg/kg in rural areas. Concentration ranges were for dioxin-like PCB toxicity equivalents (dl-PCB TEQ) from 362±164 ng/kg (industrial premises) to 6.5±1.8 ng/kg (rural areas), and for PCDD/PCDF TEQ from 503±448 ng/kg to 2.4±0.13 ng/kg. Area concentrations of PCB6 (0.040 µg/m^2 – 22 µg/m^2), dl-PCB TEQ (0.0038 ng/m^2 – 2.6 ng/m^2) and PCDD/PCDF TEQs (14 pg/m^2 – 1980 pg/m^2) were estimated. Furthermore, particle size related concentrations of PCBs and PCDD/PCDFs in street dusts were analysed showing throughout almost all samples a distinctive trend of increasing concentrations with decreasing particle sizes. Characterization of homologue patterns of PCBs and PCDDs/PCDFs in street dusts was performed showing a dependence of homologue patterns on different area types, especially for PCBs. It could be demonstrated that the analysis of concentrations in combination with specific homologue patterns of PCBs and PCDDs/PCDFs in street dust samples enables allocation of potential emission sources. However it could not be clearly pointed out that a correlation between sampling site category and concentration exists. For future research a more significant differentiation between sampling site category and concentration may be possible with a higher number of sampling points in a follow-up study.

Dusts with origin from industrial sites exhibit concentrations that can even be regarded as secondary sources for the distribution of POPs causing transfer and redeposition into their neighbourhood in the form of hot spots. NRW as an industrial federal state of Germany is affected by a significant number of recycling facilities that deal with, e.g., the recycling of transformers. Revision of regulation EC 850/2004 in order to minimize the threshold value for POPs in waste materials or as in this case in industrial dusts enables discharge of hazardous and highly contaminated materials at an earlier stage and reduces the potential for emission into the environment.

Zusammenfassung

In dieser Arbeit wurden Screening-Methoden zur Untersuchung von polychlorierten Biphenylen (PCBs), polychlorierten Dibenzo-p-dioxine und Dibenzofurane (PCDD/PCDFs) in Straßenstaub und Wischproben validiert und in der Umweltüberwachung oder als Teil von behördlichen Inspektionsprogrammen eingesetzt. Generell wurde die instrumentelle Analytik auf die Kopplung von Gaschromatographie mit hochauflösender Massenspektrometrie gestützt und die Quantifizierung wurde anhand der Isotopenverdünnungsanalyse (IDA) durchgeführt.

Straßenstaubproben wurden mit Hilfe von Handfegern mit Naturborsten und Kehrschaufeln aus Edelstahl gewonnen. Als Kriterium zur Untersuchung der Probenahmeeffektivität wurden die Massenwiederfindungen von feinteiligem Seesand (Staubsurrogat) auf Asphalt- wie auf Betonböden untersucht. Hierbei wurden höhere Massenwiederfindungen auf dem Betonuntergrund gegenüber dem Asphaltuntergrund ermittelt.

Eine Methode zur Wischprobenahme mit Hilfe von lösungsmittelgetränkten Baumwolltüchern wurde für die Untersuchung von Transfereffizienzen während der Probenahme von PCBs und PCDD/PCDFs in Feststoffbeaufschlagungen (PFs) und öligen flüssigen Filmen (OFs) bewertet. Für Feststoffbeaufschlagungen wurden hinreichende Transfereffizienzen für 1g/m^2 dotiertem mit PCB und PCDD/PCDF Kongeneren in niedriegen Konzentrationen belastetem Surrogat nach dem ersten Wischdurchgang mit n-Hexan als Lösungsmittel erzielt. Die Dotierungsexperimente für OFs zeigten eine log-lineare Korrelation zwischen der Anzahl an Wischdurchgängen und der Transfereffizienz, die auf konstante Transfereffizienzen von Wischdurchgang zu Wischdurchgang hinweisen.

Für die Extraktion von PCB und PCDD/PCDF aus Straßenstaub wurde eine Extraktionstemperaturoptimierung für die PLE Methode entwickelt und mit der Soxhlet-Extraktion für die Bestimmung von PCB in realen Straßenstaubproben verglichen. Toluol diente für beide Extraktionstechniken als Lösungsmittel. Während dieser Arbeit erzielte eine Kombination aus Toluol und PLE bessere Extraktionsausbeuten als Soxhlet-Extraktion. Die Leistungsfähigkeit der PLE Methode wurde anhand der Analyse von PCB und PCDD/PCDF in NIST (National Institute for Standards and Technology) Standard Reference Material 1649a bewertet. Hier konnte gezeigt werden, dass die Richtigkeit der PLE Methode für die Bestimmung beider Substanzklassen zufriedenstellend ist. Zusätzlich konnte gezeigt werden, dass PLE auch ein geeignetes Extraktionswerkzeug für Wischproben ist. Die Anwendbarkeit

der Wischprobenahme wurde anhand von Wischproben von nicht porösen Oberflächen verschiedenen Ursprungs aufgezeigt und die dabei ermittelten Konzentrationen an PCB ((PCB6: 0.0062 (Fensteraußenfläche eines Wohnhauses) – 1408 µg/m^2 (Arbeitsbereich eines Betriebs für Transformatorenrecycling); dioxinähnlichen PCBs (dl-PCB TEQs): 0.00072 (Fensteraußenfläche eines Wohnhauses) – 34 ng/m^2 (Arbeitsbereich eines Betriebs für Transformatorenrecycling)) und PCDD/PCDF TEQs (0.00045 (Fensteraußenfläche eines Wohnhauses) – 1614 ng/m^2 (nach Großbrand)) in den Wischproben wurden diskutiert.

Straßenstaubproben wurden aus ländlichen, städtischen, industriell beeinflussten städtischen und industriellen Bereichen genommen. PCB6 Belastungen reichten von 5090±2200 µg/kg (Mittelwert+Standardfehler des Mittelwertes) in industriellen Stäuben zu 29±8.7 µg/kg in ländlichen Bereichen. Für die dl-PCB TEQs wurden toxizitätsäquivalente Belastungen von 362±164 ng/kg (industrielle Bereiche) und 6.5±1.8 ng/kg (ländliche Bereiche) gefunden, sowie PCDD/PCDF TEQs von 503±448 ng/kg und 2.4±0.13 ng/kg. Flächenbelastungen wurden für PCB6 (0.040 µg/m^2 – 22 µg/m^2), dl-PCB TEQs (0.0038 ng/m^2 – 2.6 ng/m^2) und PCDD/PCDF TEQs (14 pg/m^2 – 1980 pg/m^2) abgeschätzt. Des Weiteren wurden korngrößenabhängige Konzentrationen von PCBs und PCDD/PCDFs in Straßenstäuben untersucht, die in nahezu allen Proben einen deutlichen Trend von zunehmenden Konzentrationen mit der Abhnahme der Partikelgröße aufzeigen. Die Charakterisierung der Homologenprofile von PCBs und PCDD/PCDFs im Straßenstaub zeigte unterschiedliche Homologenprofile für die verschiedenen Probenahmegebiete, was am deutlichsten für die PCBs zu erkennen war. Es konnte aufgezeigt werden, dass die Analyse von Konzentrationen in Kombination mit spezifischen PCB und PCDD/PCDF Homologenprofilen die Zuordnung zu potentiellen Emissionsquellen ermöglicht. Allerdings konnte nicht klar belegt werden, dass es eine Korrelation zwischen der Probenahmekategorie und den ermittelten Konzentrationen gibt. Für zukünftige Untersuchungen könnte eine signifikantere Abgrenzung zwischen Probenahmekategorie und Konzentration ermöglicht werden, wenn eine Folgestudie mit erhöhter Probenanzahl durchgeführt würde.

Stäube von industriellen Flächen weisen Konzentrationen auf die man sogar als sekundäre Quelle für die Verteilung von POPs betrachten kann, und die durch Transfer und Redeposition in ihre direkte Umgebung „hot spots“ erzeugen. NRW als industriell geprägtes Bundesland weist eine signifikante Anzahl von Recyclingbetrieben auf, die bspw. mit dem Recycling von Transformatoren beschäftigt sind. Eine Überarbeitung der Vorschrift EG850/2004 zur Minimierung des Grenzwertes von POPs in Abfällen oder wie in diesem Fall

in industriellen Stäuben, könnte eine Ausschleusung von gefährlichem und hoch belasteten Materialien zu einem früheren Zeitpunkt ermöglichen, was das Potential für eine Emission in die Umwelt vermindert.

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List of Abbreviations

%	Percent
°C	Degree celcius
µg	Microgram
µL	Microlitre
µm	Micrometre
^{12}C	Native carbon istope
$^{13}C_{12}$	Isotope labeled carbon
a	y-axis intercept
A	Area
A_c	Area concentration
$AgNO_3$	Silver nitrate
ASE	Accelerated Solvent Extraction
avg.	Average
b	Slope
BAM	Bundesanstalt für Materialforschung und –prüfung
BBodSchV	Bundesbodenschutzverordnung
BImSchV	Bundesimmissionsschutzverordnung
BZ	Ballschmiter/Zell-Number
c_m	Mass concentration
CRM	Certified reference material
CS1-5	Calibration solution 1-5

c_{TE}	Toxicity equivalent concentration
DDT	dichlorodiphenyltrichloroethane
DecaCB	Decachlorobiphenyl
dl-PCBs	Dioxin-like polychlorinated biphenyls
EC	European Commission
EN	European Standards
ESR	Electronic scrap recycling
eV	Electron volt
FC5311	Perfluorophenanthrene
g	Gram
GC	Gas chromatograph / Gas chromatography
h	Hour
H_2SO_4	Sulfuric acid
HeptaCBs	Heptachlorobiphenyls
HexaCBs	Hexachlorobiphenyls
HpCDD	Heptachlorodibenzo-p-dioxins
HpCDF	Heptachlorodibenzofurans
HRMS	High resolution mass spectrometry
HWIP	Hazardous waste incineration plant
HxCDD	Hexachlorodibenzo-p-dioxins
HxCDF	Hexachlorodibenzofurans
I	Industrial
I.D.	Inner diameter

IDA	Isotope dilution analysis
I-TE	International toxicity equivalent
kg	Kilogram
km	Kilometer
L	Litre
LANUV NRW	North Rhine-Westphalian State Agency for Nature, Environment, and Consumer Protection
ln	Natural logarithm
LOD	Limit of detection
LOQ	Limit of quantification
LRMS	Low resolution mass spectrometry
m/z	Mass to charge ratio
m^2	Square metre
m^3	Cubic metre
m_i	Mass
mL	Millilitre
mm	Millimetre
MR	Metal recycling
n	Amount of measurements
NaOH	Sodium hydroxide
NATO/CCMS	North Atlantic Treaty Organization /Committee on the Challenges of Modern Society

ng	Nanogram
NIST	National Institute of Standards and Technology
NonaCBs	Nonachlorobiphenyls
NRW	North-Rhine Westphalia
OCDD	Octachlorodibenzo-p-dioxin
OCDF	Octachlorodibenzofuran
OctaCBs	Octachlorobiphenyls
OFs	Oily liquid films
p	Significance value
PAHs	Polyaromatic hydrocarbons
PCB #101	2,2′,4,5,5′-Pentachlorobiphenyl
PCB #105	2,3,3′,4,4′-Pentachlorobiphenyl
PCB #114	2,3,4,4′,5-Pentachlorobiphenyl
PCB #118	2,3′,4,4′,5-Pentachlorobiphenyl
PCB #123	2,3′,4,4′,5′-Pentachlorobiphenyl
PCB #126	3,3′,4,4′,5-Pentachlorobiphenyl
PCB #138	2,2′,3,4,4′,5′-Hexachlorobiphenyl
PCB #153	2,2′,4,4′,5,5′-Hexachlorobiphenyl
PCB #156	2,3,3′,4,4′,5-Hexachlorobiphenyl
PCB #157	2,3,3′,4,4′,5′-Hexachlorobiphenyl
PCB #167	2,3′,4,4′,5,5′-Hexachlorobiphenyl
PCB #169	3,3′,4,4′,5,5′-Hexachlorobiphenyl

PCB #180	2,2′,3,4,4′,5,5′-Heptachlorobiphenyl
PCB #189	2,3,3′,4,4′,5,5′-Heptachlorobiphenyl
PCB #28	2,4,4′-Trichlorbiphenyl
PCB #52	2,2′,5,5′-Tetrachlorobiphenyl
PCB #77	3,3′,4,4′-Tetrachlorobiphenyl
PCB #81	3,4,4′,5-Tetrachlorobiphenyl
PCB6	The sum of the six indicator polychlorinated biphenyls
PCB6*5	Convention for the calculation of total polychlorinated biphenyl
PCBs	Polychlorinated biphenyls
PCDD	Polychlorinated Dibenzo-p-dioxins
PCDD/PCDFs	Polychlorinated Dibenzo-p-dioxins/Polychlorinated Dibenzofurans
PCDF	Polychlorinated Dibenzofurans
PeCDD	Pentachlorodibenzo-p-dioxins
PeCDF	Pentachlorodibenzofurans
PentaCBs	Pentachlorobiphenyls
PFs	Particulate films
pg	Pictogram
PLE	Pressurized liquid extraction
POPs	Persistent organic pollutants
R	Rural
r^2	Correlation coefficient

sec	Second
SOCs	Semivolatile organic compounds
SPME	Solid-phase micro extraction
SR	Social room
SRM	Standard reference material
TCDD	Tetrachlorodibenzo-p-dioxins
TCDF	Tetrachlorodibenzofurans
TDHW	Temporal deposit of hazardous waste
TEF	Toxicity equivalent factor
TEQ	Toxicity equivalent
TetraCBs	Tetrachlorobiphenyls
TR	Transformer recycling
TriCBs	Trichlorobiphenyls
TSPD	Total suspended atmospheric deposition
U	Urban
UI	Industrially influenced urban
UNEP	United Nations Environmenral Protection
UO	Used oils
US EPA	United States Environmental Protection Agency
v:v	Volume to volume ratio
VDI	The Association of German Engineers
WA	Working area

WHO	World Health Organization
WHO-TEQ	World Healts Organization-Toxicity equivalent
WS	Window surfaces
XAD	styrene/divinylbenzene co-polymer resin

1. General Introduction

1.1 Persistent organic pollutants

Persistent organic pollutants (POPs) are organic carbon-based substance classes that are released in part in large quantities into the environment as a consequence of human activity. Once released into the environment those substances remain due to their physical and chemical properties in the environment for long periods of time. Typically the term POPs is applied to halogenated pesticides (e.g., aldrin, chlordane, endrin, hexachlorobenzene), industrial chemicals (e.g., polychlorinated biphenyls) and undesired by-products (e.g., polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/PCDFs)) (see **Table 1**). The main exposure route for humans to POPs can be attributed to the accumulation of those substances in the fatty tissue of mammals in the food chain. Once accumulated through the food chain some of the POPs regulated in the POP convention (Stockholm Convention on Persistent Organic Pollutants, 2009) are described to cause multiple adverse health effects that can reach to the point of being carcinogenic.

In the following the substance classes of PCDD/PCDFs and PCBs that are in the focus of this work are introduced in more detail.

Table 1 Overview of the 12 initial POPs under the Stockholm Convention [Stockholm Convention on Persistent Organic Pollutants (POPs). Stockholm, 2009]

Pesticides	**Industrial chemicals**	**by-products**
Aldrin	Hexachlorbenzene	Hexachlorbenzene
Chlordane	PCBs	PCDD/PCDFs
DDT (dichlorodiphenyltrichloroethane)		
Dieldrin		
Endrin		
Heptachlor		
Hexachlorbenzene		
Mirex		
Toxaphene		

1.2 Polychlorinated Dibenzo-p-dioxins and dibenzofurans (PCDD/PCDFs)

The most serious accident concerning PCDD/PCDFs has taken place in Seveso (Northern Italy) in 1976. A thermal runaway during the production of trichlorophenol caused a massive release of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/PCDFs), especially 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD). At the latest, from that point on the group of PCDD/PCDFs came into the focus of public interest. Structurally, this group of organic halogenated compounds can be characterized as tricyclic, almost planar aromatic molecules, that have at least one and up to eight hydrogen atoms substituted by chlorine. In **Figure 1** the basic chemical structures of PCDDs and PCDFs are exemplarily shown.

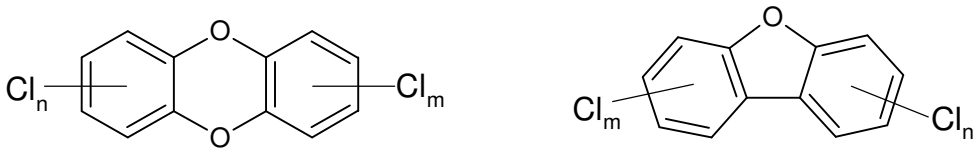


Figure 1 Chemical structures of polychlorinated Dibenzo-p-dioxins (PCDDs; left) and polychlorinated Dibenzofurans (PCDFs; right)

Table 2 Distribution of possible PCDD and PCDF congeners with respect to the homologue group.

Number of chlorine atoms	PCDD	PCDF
1	2	4
2	10	16
3	14	28
4	22	38
5	14	28
6	10	16
7	2	4
8	1	1
total	75	135

Overall the group of PCDDs and PCDFs consist of 75 and 135 different congeners, respectively. Congeners are single single compounds that are related in term of basic structur to their mentioned substance class (see **Table 2**). Congeners that exhibit the identical amount of chlorine substituents are defined as homologues. Due to their extraordinarily high

persistence in the context of chemical or biological degradation reactions, their ability to undergo long-range transport, their high toxicity in the environment and biota, PCDD/PCDFs were thereupon registered in the Stockholm Convention of Persistent Organic Pollutants (POPs) [Stockholm Convention on Persistent Organic Pollutants, 2009]. With the view on toxicological aspects the congeners that are chlorine substituted at position 2,3,7,8 are considered to be the most relevant ones. Table 3 provides an overview of those 17 congeners that fulfill this criterion. For an appropriate comparison of the toxic character of PCDD/PCDFs in environmental samples or biota a relative toxicity equivalent factor (TEF) system related to the most toxic congener TCDD has been introduced (see Table 3). There are diverse systems existing that are applied with respect to an action, target or threshold value established for the matrix in which those substances shall be evaluated. In order to generate a toxic equivalent for an environmental or biota sample the concentrations of the single 2,3,7,8 chlorine substituted congeners are multiplied with their specific TEFs and added together (**Equation 1**).

$$c_{TE} = \sum_{i}^{j} m_i * TEF_i$$

Equation 1 Calculation of toxicity equivalents in environmental or biota samples. with m_i= mass concentration of congener i; c_{TE}=total concentration in TEQ

Table 3 Overview of diverse system for the evaluation of toxicity equivalents on the basis of diverse toxicity equivalence factors

PCDD/PCDF	I-TE [NATO/CCMS, 1988; Kutz et al., 1990]	WHO 1998 [van den Berg, 1998]	WHO 2005 [van den Berg, 2006]
2,3,7,8-TCDD	1	1	1
1,2,3,7,8-PeCDD	0.5	1	1
1,2,3,4,7,8-HxCDD	0.1	0.1	0.1
1,2,3,6,7,8-HxCDD	0.1	0.1	0.1
1,2,3,7,8,9-HxCDD	0.1	0.1	0.1
1,2,3,4,6,7,8-HpCDD	0.01	0.01	0.01
OCDD	0.001	0.0001	0.0003
2,3,7,8-TCDF	0.1	0.1	0.1
1,2,3,7,8-PeCDF	0.05	0.05	0.03
2,3,4,7,8-PeCDF	0.5	0.5	0.3
1,2,3,4,7,8-HxCDF	0.1	0.1	0.1
1,2,3,6,7,8-HxCDF	0.1	0.1	0.1
1,2,3,7,8,9-HxCDF	0.1	0.1	0.1
2,3,4,6,7,8-HxCDF	0.1	0.1	0.1
1,2,3,4,6,7,8-HpCDF	0.01	0.01	0.01
1,2,3,4,7,8,9-HpCDF	0.01	0.01	0.01
OCDF	0.001	0.0001	0.0003

1.3 Polychlorinated Biphenyls (PCBs)

Another important group of strictly regulated toxic chemicals are PCBs. They are often investigated together with PCDD/PCDFs, for example in the monitoring network of air quality in North Rhine-Westphalia. This substance class of chlorinated aromatic hydrocarbons comprises altogether 209 compounds with different positions and number of chlorine substituents at the biphenyl backbone. As in the systematic nomenclature of PCDD/PCDFs the single compounds are called congeners and those congeners that exhibit the same number of chlorine substituents in the molecule are described as homologues. In contrast to PCDD/PCDFs, PCBs were purposefully produced in huge industrial scale for diverse fields of application. PCBs were used on the one hand as technical mixtures in closed applications, e.g., in transformers or capacitors and on the other hand in open applications as additives, e.g., in sealing materials, paints or hydraulic oils. After the first serious health effects became clear, massive regulations and prohibitions for the handling of PCBs were introduced. In Germany the use of PCB in open applications was prohibited in 1978 followed by a total stop of PCB production in 1989 [Verbot des Inverkehrbringens von PCB, 1978; Verordnung zum Verbot, 1989]. Consequently, due to their comparable chemical structure and environmental behaviour to PCDD/PCDFs, PCBs were included in the Stockholm Convention on POPs [Stockholm Convention on Persistent Organic Pollutants, 2009] at international level. To be specific this is true for those 12 out of the 209 congeners that are from a toxicological point of view relevant and which are consequently defined as dioxin-like PCBs (dl-PCBs). The evaluation of the toxicity in environmental and biota samples is ensured by the adaptation of individual TEF for the dl-PCBs [van den Berg et al., 1998 and 2006]. An overview of TEF established by the WHO can be seen in Table 4**.**

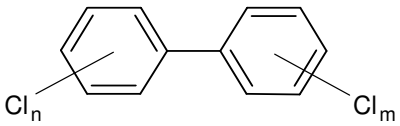


Figure 2 Chemical structures of polychlorinated biphenyls (PCBs)

Furthermore, Ballschmiter and Zell suggested a simple system to designate the single congeners with numbers from #1 to #209 [Ballschmiter and Zell, 1980]. This nomenclature is well accepted and prevails until today. Next to the toxicologically relevant dl-PCBs the so called indicator-PCBs (PCB #28, #52, #101, #138, #153, #180) are additionally of analytical and regulative interest since several action, target or threshold values are based on the single congeners, the sum of those six congeners or on the sum of those six congeners times five. Those six congeners are the most abundant congeners in commercially PCB formulations. Regulations are established for diverse matrices such as food, soil, waste, waste oil or surface contaminations [Altölverordnung, 2002; BBodSchV, 1990; Regulation 850/2004/EC, 2004; Kontaminanten-Verordnung, 2010; US EPA 761.125, 2007].

Table 4 Overview of the WHO systems for the evaluation of toxicity equivalents on the basis of diverse toxicity equivalence factors for PCBs. BZ=Ballschmiter-Number.

PCB	BZ #	WHO 1998 [van den Berg et al., 1998]	WHO 2005 [van den Berg et al., 2005]
3,4,4',5-Tetrachlorobiphenyl	81	0.0001	0.0003
3,3',4,4'-Tetrachlorobiphenyl	77	0.0001	0.0001
3,3',4,4',5-Pentachlorobiphenyl	126	0.1	0.1
3,3',4,4',5,5'-Hexachlorobiphenyl	169	0.01	0.03
2',3,4,4',5-Pentachlorobiphenyl	123	0.0001	0.00003
2,3',4,4',5-Pentachlorobiphenyl	118	0.0001	0.00003
2,3,4,4',5-Pentachlorobiphenyl	114	0.0005	0.00003
2,3,3',4,4'-Pentachlorobiphenyl	105	0.0001	0.00003
2,3',4,4',5,5'-Hexachlorobiphenyl	167	0.00001	0.00003
2,3,3',4,4',5-Hexachlorobiphenyl	156	0.0005	0.00003
2,3,3',4,4',5'-Hexachlorobiphenyl	157	0.0005	0.00003
2,3,3',4,4',5,5'-Heptachlorobiphenyl	189	0.0001	0.00003

Table 5 Distribution of possible PCB congeners with respect to the homologue group.

Homologue	Number of Chlorine atoms	PCB
Monochlorobiphenyl	1	3
Dichlorobiphenyl	2	12
Trichlorobiphenyl	3	24
Tetrachlorobiphenyl	4	42
Pentachlorobiphenyl	5	46
Hexachlorobiphenyl	6	42
Heptachlorobiphenyl	7	24
Octacholorobiphenyl	8	12
Nonachlorobiphenyl	9	3
Decachlorobiphenyl	10	1
	total	209

1.4 Exposure of PCDD/PCDFs and PCBs to the environment

PCDD/PCDFs are substances which have never been produced intentionally man-made and were at no time utilized for technical formulations. In fact PCDD/PCDF can be observed as by-products in industrial processes, namely thermic processes in which organic matter and chlorine are present. The formation of PCDD/PCDFs is promoted if precursor substances such as chlorinated phenols, biphenyls, diphenylethers or benzenes are involved in industrial processes of up to 800°C [Rappe and Marklund, 1978; Buser, 1979a; Buser, 1979b]. This type of source for PCDD/PCDF originating from processes and products concerning the chemistry of halogen compounds was recognized to be the major pathway for PCDD/PCDFs into the environment in the 1960s and 1970s. However, with the beginning of the 1970s additional major source of PCDD/PCDFs for the environment emerged. This is evident for diverse combustion processes. Here, primary emissions of those generally non-volatile substances are caused by municipal waste incinerators [Fiedler and Hutzinger, 1978, Domingo et al., 2001], metallurgical processes for the primary production of metals (sintering plants) [Buekens et al., 2001], recycling processes of scrap metals, domestic heating or accidental heavy fires. PCDD/PCDFs originate as a mixture according to their source. The comparison of PCDD/PCDF congener and/or homologue profiles for the identification of a specific source can be performed by means of the congener and homologue specific profiles [Domingo et al., 2001, Cheng et al., 2003]. Due to the fact that PCDD/PCDFs are mostly emitted into the

atmosphere, intensive national and international regulations on primary PCDD/PCDF emissions were introduced, e.g., for waste incineration plants, sintering plants or further potential industrial sites with a limit value of 0.1 ng I-TE/m^3 in 1990 [NATO/CCMS, 1988; 17. BImSchV, 2013; Directive 2000/76/EC; 2000] leading to a successful reduction of emissions [Bruckmann et al., 2013]. Partitioning between gas phase and particles plays an important role for the atmospheric transport of those semivolatile organic compounds [Lohmann et al., 2000; Mandalakis et al., 2002]. The major removal processes from the atmosphere can be attributed to gaseous, wet and particulate deposition processes. The Federal State Committee for Immission Control of Germany introduced a target value for PCDD/PCDFs in the atmospheric deposition and ambient air [Bericht des Länderausschusses für Immissionsschutz; 2004]. The target value for atmospheric deposition is 4 pg WHO-TEQ m^2/day and for ambient air a maximum target value of 150 fg WHO-TEQ/m^3 was introduced. In North Rhine-Westphalia a monitoring network for PCDD/PCDF atmospheric depositions and concentrations of PCDD/PCDFs in ambient air has been running since 1988. PCDD/PCDF concentrations in ambient air in general meet the target value of 150 fg TEQ-WHO/m^3 but the target value for atmospheric deposition is still exceeded (Bruckmann et al., 2013).

In contrast to PCDD/PCDFs, PCBs were intentionally produced for diverse fields of application. The primary emission via the gas phase can be neglected nowadays. During the time of PCB production large quantities of the world wide produced PCB formulations were used in open applications as aforementioned. As a consequence of the excessive use those chemicals are ubiquitously distributed in the environment. Nowadays, secondary sources for PCBs mainly present in the industrial sector have come into the focus. As an excellent example for a secondary source of PCBs the identification of a PCB emitting recycling company in the harbor area of Dortmund can be mentioned [Bruckmann et al., 2011].

1.5 Analysis of POPs in environmental sample

1.5.1 Active and passive sampling of POPs

The first decisive step during the analysis of POPs like PCBs, dl-PCBs and PCDD/PCDFs is an appropriate and efficient sampling technique. This is not only true for the sampling of organics but also for the sampling of inorganics in diverse matrices. An appropriate and efficient sampling technique requires that the technique applied to a certain matrix yields representative results and should allow problem-oriented conclusions. Furthermore, in order to safe time, money and training sampling methods should be as simple as possible.

Basically two different sampling approaches are normally applied to POPs analysis, differentiating in active and passive sampling techniques. Active sampling is a classical and conventional sampling method for the collection of POPs in ambient air. In Europe the standard method adopted for the environmental monitoring of PCDD/PCDFs and PCBs in ambient air and for the surveillance of industrial activities possibly emitting those component classes is based on low-, medium- or high-volume samplers [EN 1948-1, 2006; EN 1948-4, 2010; Dong et al., 2015]. This sampling technique is often adapted to other substance classes regulated, e.g., other halogenated organic pollutants. Due to the need of electricity for the operation of a pumping system and safety installations during active sampling of ambient air and its relatively vast footprint required passive sampling systems for the monitoring of indoor air and ambient air have been gaining interest over the last years [Hazrati and Harrad, 2007; Bohlin et al., 2014]. Polyurethane foam and XAD (styrene/divinylbenzene co-polymer) resin based passive sampler systems were extensively studied and applied. For those sampler types undesired long exposure times of up to three months are required to collect a quantifiable amount of POPs for chemical analysis [Xu et al., 2013]. POPs in liquid matrices can be passively sampled using solid-phase microextraction (SPME) devices. Those systems are often applied to measure dissolved concentrations of chemicals in the liquid phase. However, especially for POPs the solubility in water is extremely low, so that undesired matrix components with comparable polarity can ad- or absorb to the SPME polymer over the long exposure time and cause additional problems for the analysis [Kot-Wasik et al., 2007]. Next to the passive sampling of POPs in the gaseous and liquid phase the use of naturally occurring matrices has been addressed for the assessment of the status of contamination in the past years as passive sampling systems. Biomonitors as living organisms represent an important group of naturally occurring passive samplers for the assessment of air pollution or atmospheric deposition. In this context the most commonly applied biomonitors are lichens,

mosses, pine needles and plants. To give an example, a PCB source in North Rhine-Westphalia was allocated by the exposure of green cabbage as a passive sampler by the North Rhine-Westphalian State Agency for Nature, Environment, and Consumer Protection (LANUV NRW) [Radermacher et al. 2011].

Impervious surfaces play an important role in the fate of potentially toxic contaminants in the environment. Transfer of POPs, emitted in the gaseous state like PCBs and PCDD/PCDFs, from the atmosphere to terrestrial natural impervious surfaces occurs predominantly through atmospheric deposition processes. Processes of gaseous, wet and dry particulate deposition have been extensively characterized in the last decades [Eitzer and Hites, 1989; Jones and Duarte-Davidson, 1997]. Sampling of atmospheric deposition is done by special and partly complex sampling equipment. A glass funnel-bottle bulk collector, stainless steel buckets, funnels connected to absorber cartridge systems were used for the collection of polyaromatic hydrocarbons (PAHs), PCBs and PCDD/PCDFs and described in the literature [Amodio et al., 2014]. The VDI (The Association of German Engineers) suggests exposure of glass jars for the collection of PCDD/PCDFs for four weeks [VDI 2090-Part 1; 2001]. The application of such a sampling technique does often not allow obtaining quickly information on the contamination situation in cases of environmental monitoring of POPs. Therefore, naturally occurring environmental matrices such as those deposited on surfaces have come into focus for the assessment of the status of contamination in the past years [Yang and Baumann, 1996; de Miguel et al., 1997; Loganathan et al., 1997; Irvine and Loganathan, 1998; Zakaria et al., 2002; Bruckmann et al., 2011; Li et al., 2013; Wang et al., 2013]. In the current work the main focus was set on the determination of PCBs and PCDD/PCDFs in street dust and wipe samples taken from impervious surfaces.

1.5.2 Sample preparation

1.5.2.1 Extraction of POPs from environmental matrices

Sample preparation involving extraction is a critical step during the analysis of organics like POPs in environmental samples, since it is time-consuming and susceptible for errors and loss of analytes. In this context Soxhlet extraction was the most common and exhaustive extraction technique over the last decades. Despite the fact that Soxhlet extraction is time consuming and requires large amounts of solvent the extraction of POPs from solid matrices like soil, sediments or even street dust is still routinely performed by using classical standard Soxhlet extraction. For example, street dust samples investigated by Irvine and Loganathan

(1998) were Soxhlet-extracted for the determination of PCBs. The use of alternative extraction techniques like supercritical fluid extraction, microwave assisted extraction, ultrasonication extraction and pressurized liquid extraction (PLE) became more and more popular during the last decades [Bowadt and Hawthorne, 1995; Ramos et al., 2002; Basheer et al., 2005; Sporring et al., 2005]. Exemplarily, Sporring et al. (2005) concluded that any of those techniques aforementioned can be successfully used for the extraction of PCBs from soil if the extraction parameters applied for the specific technique are chosen properly. In addition, the extraction of PCBs and PCDD/PCDFs from street dust or wipe samples in this study should be performed more economically and ecologically. In this study the focus was set to the extraction of selected POPs using PLE. A schematic overview of PLE can be seen in **Figure 3**. For PLE stainless steel extraction cells are loaded with the desired solid sample. Typically for PLE, the extraction of environmental matrices is performed with organic solvents at high temperature placed in a temperature adjustable oven. The temperatures used for PLE typically exceed the boiling point of the used solvent, which is kept in liquid state by the applied high pressure. As a consequence of high temperature, faster analyte desorption from the matrix is observed. Several parameters, like temperature, pressure, extraction time, solvent and extraction cycles are influencing the PLE extraction efficiency of organic compounds. However, next to the choice of an appropriate solvent, extraction temperature is known to have the largest influence on the extraction efficiency [Richter et al., 1997]. As a positive consequence if PLE can be routinely used the consumption of high-grade organic solvents is reduced and the extraction times can be dramatically shortened.

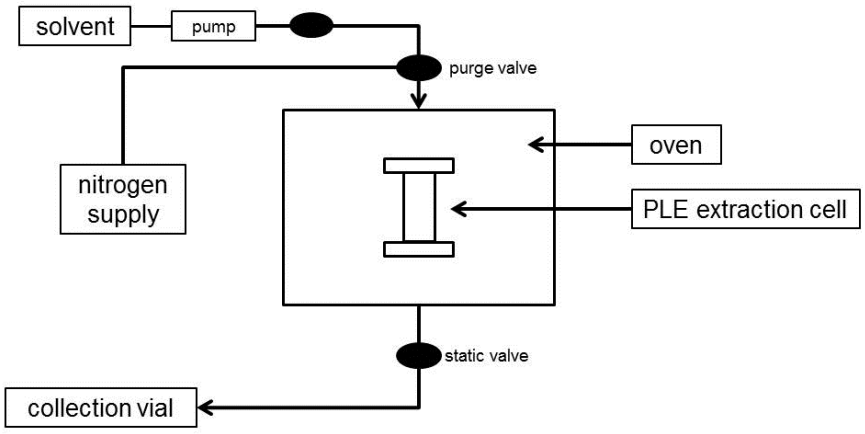


Figure 3 Schemtaic overview of pressurized liquid extraction

1.5.2.2 Clean-up and separation during POP analysis

Extraction of environmental samples results in extracts that cannot be directly analyzed. Due to large amounts of co-extracted interfering substances chromatographic separation and/or detection can be disturbed or even made impossible. The most common way to clean-up crude sample extracts is the application of column chromatography based on neutral, acidic or basic silica [Xu et al., 2013]. To avoid ambiguous results due to co-elutions during chromatographic runs, the separation of halogenated POPs into component specific analyte fractions is necessary. For those separations active carbon and alumina were established to show good results [EN 1948-4, 2010; Xu et al., 2013].

1.5.2.3 Instrumental analysis

PCDD/PCDFs and PCBs are mostly analysed via high resolution gas chromatography (HRGC) coupled to high resolution mass spectrometry (HRMS) in environmental samples. Hereby quantification is performed by isotope dilution analysis (IDA) using $^{13}C_{12}$-labeled 2,3,7,8 chlorine substituted internal standards. Basically for each native ^{12}C-equivalent that shall be analyzed in an environmental matrix a $^{13}C_{12}$-labeled isotope standard is required. One should note that exceptions can occur as it can be seen in the quantification scheme for the determination of PCDD/PCDFs in stack gas samples [EN 1948-3, 2006]. At different stages of the analytical protocol, e.g., before sampling, as a mixture of $^{13}C_{12}$-labeled isotope standards for the quantification before extraction or as recovery standard just after the last

sample preparation step before injection into the chromatographic system, $^{13}C_{12}$-labeled isotope standards can be added to the sample. $^{13}C_{12}$-labeled isotope standards behave physically and chemically comparable to their ^{12}C-equivalents, which are the target analytes in environmental samples. Thus, possible losses of the analytes of interest during the complete analytical procedure are automatically balanced. Hence, quality aspects such as recovery rates can be easily monitored [EN 1948-1, 2006; EN 1948-2, 2006; EN 1948-3, 2006; EN 1948-4, 2010]. Quantification is actually based on the comparison of the peak areas between the ^{12}C-equivalent in the sample and the $^{13}C_{12}$-labeled isotope standards spiked before extraction. This relationship is depicted in Equation 2.

$$c_i = \frac{A_i}{A_{STD}} * c_{STD} * \frac{1}{rRf}$$

Equation 2. Calculation of mass concentration of ^{12}C-equivalents in the sample solution. With c_i= mass concentration of the native congener in the sample solution; c_{STD}= mass concentration of the $^{13}C_{12}$-labeled isotope standard congener spiked before extraction; A_i= peak area of the native congener in the sample solution; A_{STD}= mass concentration of the $^{13}C_{12}$-labeled isotope standard congener spiked before extraction in the sample solution; rRf= relative response factor of the native congener calculated from an calibration solution

In dependence on a relative response factor (rRf) the mass concentration of the analyte can be calculated in the sample solution. The rRfs for each single native congener are determined in a separate analytical run (external calibration). They describe the analytical response between the ^{12}C-equivalents in the sample and the $^{13}C_{12}$-labeled isotope standard.

$$rRf = \frac{A_i}{A_{STD}} * \frac{c_{STD}}{c_i}$$

Equation 3. Calculation of a relative response factor for ^{12}C-equivalents in calibration solutions.

1.6 Scope of this thesis

The scope of this thesis was to investigate and to validate sampling procedures and sample preparation steps for the determination of persistent organic pollutants like PCBs and PCDD/PCDFs in surface samples, to be more specific for the surface matrices street dust and wipe samples. The focus of the sampling methods developed during this work was set to be as simple as possible in order to avoid heavy maintenance and training for laboratory staff by being as quantitative as possible. During environmental emergencies, in governmental monitoring programs or for the general increase of sample throughput in laboratories, extraction of PCBs and PCDD/PCDFs from any kind of matrix is in the most cases the bottle-neck in overall analysis time. To overcome this problem PLE as an alternative extraction method for PCBs and PCDD/PCDFs from street dusts and wipe samples was investigated.

In **Chapter 2** the development and validation of an analytical method for the determination of PCBs and PCDD/PCDFs in street dust samples is described. As part of the overall analytical method validation a simple and quantitative method for the sampling of street dust was investigated. In addition, toluene was tested as extraction solvent for PCBs and PCDD/PCDFs.

In **Chapter 3** the main focus was on the application of the analytical method developed in Chapter 2. Here the intention was to use street dust as an easily accessible passive sampling matrix that can be used to trace back industrial contaminations. Next to the investigation of the correlation of PCB and PCDD/PCDF concentrations and area loads with particle size fractions, differences in concentrations with respect to sampling site categories such as rural or urban were evaluated using chemometric tools.

The main focus of **Chapter 4** was on the method development and validation for the determination of PCBs and PCDD/PCDFs in wipe samples. An integral part of this chapter was to examine wipe sampling transfer efficiencies of individual low concentrated PCB and PCDD/PCDF congeners in particulate films and oily liquid films from an impervious glass surface and furthermore to explore variability in transfer efficiencies. The use of PLE for wipe samples was additionally tested during method validation.

1.7 References

Amodio, M.; Catino, S.; Dambruoso, P.R.; de Gennaro, G.; Di Gilio, A.; Giungato, P.; Laiola, E.; Marzocca, A.; Mazzone, A.; Sardaro, A.; Tutino, M. Atmospheric Deposition: Sampling Procedures, Analytical Methods, and Main Recent Findings from the Scientific Literature. Advances in Meteorology, 2014, 1-27.

Altölverordnung (AltölV). 16.04.2002.

Ballschmiter, K.; Zell, M. Analysis of polychlorinated biphenyls (PCB) by glass capillary gas chromatography. Fres. J. Anal. Chem. 1980, 302, 20-31.

Basheer, C.; Obbard, J.P.; Lee, H.K. Analysis of persistent organic pollutants in marine sediments using a novel microwave assisted solvent extraction and liquid-phase microextraction technique. J. Chromatogr. A 2005, 1068, 221-228.

BBodSchV. Bundes-Bodenschutz- und Altlastenverordnung. 12.07.1999.

Bericht des Länderausschusses für Immissionsschutz (LAI) „Bewertung von Schadstoffen, für die keine Immissionswerte festgelegt sind - Orientierungswerte für die Sonderfallprüfung und für die Anlagenüberwachung sowie Zielwerte für die langfristige Luftreinhalteplanung unter besonderer Berücksichtigung der Beurteilung krebserzeugender Luftschadstoffe“ Länderausschusses für Immissionsschutz (LAI) 61.0-06 21.09.2004.

Bohlin, P.; Audy, O.; Skrdlikova, L.;Kukucka, P; Pribylova, P.; Prokes, P.; Vojta, S. Klanova, J. Outdoor passive air monitoring of semi volatile organic compounds (SVOCs): a critical evaluation of performance and limitations of polyurethane foam (PUF) disks. Environ. Sci.: Processes Impacts, 2014, 16, 433-444.

Bowadt, S.; Hawthorne, S.B. Supercritical fluid extraction in environmental analysis. J. Chromatogr. A 1995, 703, 549-571.

Bruckmann, P.; Hiester, E.; Klees, M.; Radermacher, L. Environmental pollution by polychlorinated biphenyls (PCB) in the harbour region of Dortmund. Gefahrst. Reinhalt. der Luft 2011, 4, 151-158.

Bruckmann, P.; Hiester, E.; Klees, M.; Zetzsch, C. Trends of PCDD/F and PCB concentrations and depositions in ambient air in Northwestern Germany. Chemosphere 2013, 93, 1471–1478.

Buekens, A.; Stieglitz, L.; Hell, K.; Huang, H.; Segers, P. Dioxins from thermal and metallurgical processes: recent studies for the iron and steel industry. Chemosphere 2001, 42, 729-739.

Buser, H.R. Formation of polychlorinated dibenzofurans (PCDFs) and dibenzo-p-dioxins (PCDDs) from the pyrolysis of individual PCB isomers. Chemosphere 1979a, 8, 157-175.

Buser, H.R. Formation of polychlorinated dibenzofurans (PCDFs) and dibenzo-p-dioxins (PCDDs) from the pyrolysis of chlorobenzenes. Chemosphere 1979b, 8, 415-424.

Cheng, P-S.; Hsu, M-S.; Ma, E.; Chou, U.; Ling, Y-C. Levels of PCDD/FS in ambient air and soil in the vicinity of a municipal solid waste incinerator in Hsinchu. Chemosphere 2003, 52, 1389–1396.

de Miguel, E.; Llames, J.F.; Chacón, E.; Berg, T.; Larssen, S.; Røyset, O.; Vadset, M. Origin and patterns of distribution of trace elements in street dust: Unleaded petrol and urban lead. Atmos. Environ. 1997, 31, 2733-2740.

Directive 2000/76/EC of the European Parliament and of the council of 4 December 2000 on the incineration of waste. Official Journal of the European Communities L 332/91.

Directive 850/2004/EC of the European Parliament and board dealing with persistent organic pollutants, L 158, 30.04.2004.

Dong, Y.; Fu, S.; Zhang, Y.; Nie, H.; Li, Z. Polybrominated diphenyl ethers in atmosphere from three different typical industrial areas in Beijing, China. Chemosphere 2015, 123, 33-42.

Domingo, J.L.; Granero, S.; Schuhmacher, M. Congener profiles of PCDD/F in soil and vegetation samples collected near to a municipal waste incinerator. Chemosphere 2001, 43, 514-524.

Eitzer, B.D.; Hites, R.A. Atmospheric transport and deposition of polychlorinated dibenzo-p-dioxins and dibenzofurans. Environ. Sci. Technol. 1989, 23, 1396–1401.

EN 1948-1 Stationary source emissions - Determination of the mass concentration of PCDDs/PCDFs and dioxin-like PCBs – Part 1: Sampling of PCDDs/PCDFs; German version EN 1948-1:2006

EN 1948-2 Stationary source emissions - Determination of the mass concentration of PCDDs/PCDFs and dioxin-like PCBs- Part 2: Extraction and clean-up of PCDDs/PCDFs; German version EN 1948-2:2006

EN 1948-3 Stationary source emissions - Determination of the mass concentration of PCDDs/PCDFs and dioxin-like PCBs - Part 3: Identification and quantification of PCDDs/PCDFs; German version EN 1948-3:2006

EN 1948-4 Stationary source emissions - Determination of the mass concentration of PCDDs/PCDFs and dioxin-like PCBs – Part 4: Sampling and analysis of dioxin-like PCBs; German version EN 1948-4:2010

Fiedler, H.; Hutzinger, O. Sources and Sinks of Dioxins: Germany. Chemosphere 1978, 25, 1487-1491.

Hazrati, S.; Harrad, S. Calibration of polyurethane foam (PUF) disk passive air samplers for quantitative measurement of polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs): Factors influencing sampling rates Chemosphere 2007, 67, 448–455.

Irvine, K.N.; Loganathan, B.G. Localized enrichment of PCB levels in street dust due to redistribution by wind. Water, Air and Soil Pollution 1998, 105, 603–615.

Jones, K.C.; Duarte-Davidson, R. Transfers of Airborne PCDD/Fs to Bulk Deposition Collectors and Herbage. Environ. Sci. Technol. 1997, 31, 2937–2943.

Kontaminanten-Verordnung (KmV). 19.03.2010.

Kot-Wasik, A.; Zabiegała, B.; Urbanowicz, M.; Dominiak, E.; Wasik, A.; Namiesnik, J. Advances in passive sampling in environmental studies. Anal. Chim. Acta 2007, 602, 141–163.

Kutz, F.W.; Barnes, D.G.; Bottimore, D.P.; Greim, H.; Bretthauer, E.W. The international toxicity equivalency factor (I-TEF) method for estimating risks associated with exposures to complex mixtures of dioxins and related compounds. Chemosphere 1990, 20, 751-757.

Loganathan, B.G.; Irvine, K.N.; Kannan, K.; Pragatheeswaran, V.; Sajwan, K.S. Distribution of Selected PCB Congeners in the Babcock Street Sewer District: A Multimedia Approach to Identify PCB Sources in Combined Sewer Overflows (CSOs) Discharging to the Buffalo River, New York. Arch. Environ. Contam. Toxicol. 1997, 33, 130–140.

Lohmann, R.; Lee, R.G.M; Green, N.J.L., Jones, K.C. Gas-particle partitioning of PCDD/Fs in daily air samples. Atmos. Environ. 2000, 34, 2529-2537.

Mandalakis, M.; Tsapakis, M.; Tsoga, A.; Stephanou E.G. Gas–particle concentrations and distribution of aliphatic hydrocarbons, PAHs, PCBs and PCDD/Fs in the atmosphere of Athens (Greece). Atmos. Environ. 2002, 36, 4023–4035.

NATO/CCMS (North Atlantic Treaty Organisation/Committee on the Challenge of Modern Society) International toxicity equivalence factors (I-TEF) method of risk assessment for complex mixtures of dioxins and related compounds, 186, 1988.

Radermacher, L.; Altenbeck, P.; Kraft, M.; Delschen, T.; Hiester, E. Finding of PCB-sources in the harbour of Dortmund by exposure of vegetable bioindicators. Gefahrst. Reinhalt. der Luft 2011, 4, 159-164.

Rappe, C.; Marklund, S. Formation of polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) by burning or heating chlorophenates. Chemosphere 1978, 7, 269-281.

Richter, B.E.; Ezzell, J.L.; Knowles, D.E.; Hoefler, F.; Mattulat, A.K.R.; Scheutwinkel, M.; Waddell, D.S.; Gobran, T.; Khurana, V. Extraction of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans from environmental samples using accelerated solvent extraction (ASE). Chemosphere 1997, 34, 975-987.

17. BImSchV. Siebzehnte Verordnung zur Durchführung des Bundes-Immissionsschutzgesetzes (Verordnung über die Verbrennung und die Mitverbrennung von Abfällen - 17. BImSchV) 17. BImSchV 2013.

Sporring, S.; Bowadt, S.; Svensmark, B.; Björklund, E. Comprehensive comparison of classic Soxhlet extraction with Soxtec extraction, ultrasonication extraction, supercritical fluid extraction, microwave assisted extraction and accelerated solvent extraction for the determination of polychlorinated biphenyls in soil. J. Chromatogr. A 2005, 1090, 1-9.

Stockholm Convention on Persistent Organic Pollutants (POPs). Stockholm. 2009.;http://chm.pops.int/TheConvention/ConventionText/tabid/2232/Default.aspx

US EPA, 2007. 761.125 - Requirements for PCB spill cleanup.

van den Berg, M.; Birnbaum, L.S.; Bosveld, A.T.; Brunstrom, B.; Cook, P.; Feely, M.; Giesy, J.P.; Hanberg, A.; Hasegawa, R.; Kennedy, S.W.; Larsen, J.C.; van Leeuwen, F.X.; Liem,

A.K.; Nolt, C., Peterson, R.E.; Poellinger, L.; Safe, S.; Schrenk, D.; Tillitt, D.; Tysklind, M.; Younes, M.; Waern, F.; Zacharewski, T. Toxic equivalence factors (TEFs) for PCBs, PCDDs, PCDFs for human and wildlife. Environ. Health Perspect. 1998, 106, 775–792.

van den Berg, M., Birnbaum, L. S., Denison, M., De Vito, M., Farland, W., Feeley, M, Fiedler, H., Hakansson, H., Hanberg, A., Haws, L., Rose, M., Safe, S., Schrenk, D., Tohyama, C., Tritscher, A., Tuomisto, J., Tysklind, M., Walker, N., Peterson, R. E. The 2005 World Health Organization Re-evaluation of Human and Mammalian Toxic Equivalency Factors for Dioxins and Dioxin-like Compounds. Toxicol. Sci. 2006, 93, 223 – 241.

VDI 2090 - Part 1 Deposition measurement of low volatile organic compounds - Determination of PCDD/F deposition Bergerhoff sampling device and GC/HRMS analysis. Verein Deutscher Ingenieure, Düsseldorf 2001.

Verbot des Inverkehrbringens von PCB in offenen Systemen in Deutschland, Zehnte Durchführungsverordnung zum Bundes-Immissionsschutzgesetz, 1978.

Verordnung zum Verbot von polychlorierten Biphenylen, polychlorierten Terphenylen und zur Beschränkung von Vinylchlorid (PCB-, PCT-, VCVerbotsverordnung) vom 18.07.1989.

Wang, W.; Wu, F.; Zheng, J.; Wong, M.H. Risk assessments of PAHs and Hg exposure via settled house dust and street dust, linking with their correlations in human hair. J. Hazard Mater. 2013, 263, 627– 637.

Xu, W.; Wang, X.; Cai, Z. Analytical chemistry of the persistent organic pollutants identified in the Stockholm Convention: A review. Anal. Chim. Acta 2013, 790, 1–13.

Yang, Y.; Baumann, W. Study of polychlorinated biphenyls in street dust by supercritical fluid extraction gas chromatography/mass spectrometry. Fresenius J. Anal. Chem. 1996, 354, 56-60.

Zakaria, M.P.; Takada, H.; Tsutsumi, S.; Ohno, K.; Yamada, J.; Kouno, E.; Kumata, H. Distribution of Polycyclic Aromatic Hydrocarbons (PAHs) in Rivers and Estuaries in Malaysia: A Widespread Input of Petrogenic PAHs. Environ. Sci. Technol. 2002, 36, 1907–1918.

2. Determination of polychlorinated biphenyls and polychlorinated dibenzo-p-dioxins and dibenzofurans by pressurized liquid extraction and gas chromatography coupled to mass spectrometry in street dust samples

Redrafted from "Klees, M.; Hiester, E.; Bruckmann, P.; Schmidt, T.C. Determination of polychlorinated biphenyls and polychlorinated dibenzo-p-dioxins and dibenzofurans by pressurized liquid extraction and gas chromatography coupled to mass spectrometry in street dust samples. J. Chromatogr. A 2013, 1300, 17-23."

2.1 Introduction

In general, the term 'street dust' refers to the load of deposited dust on a paved surface. However, the term refers not only to dust that collects on surfaces next to a road, but also to dust that collects on other paved surfaces, such as at industrial sites. A critical aspect of street dust analysis is the threshold size of the dust particles considered. Yang et al. examined particle sizes of <100 µm when determining levels of PCBs in street dust [Yang and Baumann, 1997], whereas Irvine and Loganathan analysed PCB levels in particles as large as 250 µm [Irvine and Loganathan, 1998]. A broader spectrum of particle sizes than was used in these studies needs to be sampled and analysed to provide a comprehensive overview of PCB and PCDD/PCDF burdens in street dusts. This overview is necessary to identify the size ranges of the particles that contribute most to the pollution, even if they do not necessarily make the largest contribution to the mass of the sample. Given that street dust is an excellent carrier and adsorbent for many organic and inorganic trace toxic analytes [de Miguel et al., 1997; Takada et al., 1991], the occurrence of diverse trace compounds in street dust samples has been investigated extensively. To that end, several sampling techniques for street dust samples have been developed. Irvine and Loganathan used a stainless steel scoop to sample PCBs in street dust, and stored the sampled dust in pre-cleaned glass bottles prior to analysis [Irvine and Loganathan, 1998]. A small paintbrush has also been used to collect street dust

from street surfaces in order to determine levels of metals [de Miguel et al., 1997], and a vacuum cleaner was used to determine levels of polycyclic aromatic hydrocarbons (PAHs) in street dust [Takada et al., 1991]. A disadvantage of all these sampling methods is that they focus on the concentration of the analytes of interest in the sampled mass of dust. However, for the estimation of the total deposition load it is also important to know the area burden, which is the amount of sampled material on a certain sampling area. Despite its indispensability for these types of analyses, area burden has seldom been considered. The surface roughness of the sampling area plays a major role in determining the efficiency of a sampling method.

The present study involved the analysis of street dust samples for polychlorinated biphenyls (PCBs), as well as levels of polychlorinated dibenzodioxins and furans (PCDD/PCDFs). Due to recent massive pollution with PCB in the harbour area of the city of Dortmund, Germany, [Bruckmann et al., 2011] the study focused on the analysis of PCBs. Despite the great deal of work on PCBs and PCDD/PCDFs in environmental analysis, surprisingly few studies have been reported so far that specifically deal with the determination of those organic pollutants in street dust [Yang and Baumann, 1997]. In organic trace and ultra-trace analysis, several extraction techniques are used to isolate compounds of interest from solid matrices. Since the introduction of pressurized liquid extraction (PLE), this technique is often applied to environmental matrices. Conditions for PLE, such as the extraction temperature and extraction solvent, have been optimised [Schantz et al., 1997; Björklund et al., 1999; Bandh et al., 2000; Ramos et al., 2002; Harrad et al., 2006; Kiguchi et al., 2006; Zhang et al. 2011]. Schantz et al. used PLE to analyse PCBs in urban-dust standard reference material [Schantz et al., 1997; Poster et al., 1999]. In their work, dichloromethane, acetonitrile and a mixture of n-hexane/acetone (1:1, v:v) were used for PLE of the reference material. For the determination of PCBs and polybrominated diphenylethers in house-dust samples, n-hexane was used as extraction solvent in PLE [Harrad et al., 2006]. Yang et al. (1996) used supercritical fluid extraction for the extraction of PCBs in street dusts. Street dust samples investigated by Irvine and Loganathan were Soxhlet extracted for the determination of PCBs [Irvine and Loganathan, 1998]. Soxhlet extraction remains the standard method for routine analysis in many laboratories, despite the fact that its use is time consuming and requires large amounts of solvent. We therefore investigated the feasibility of simultaneous extraction and determination of PCBs and PCDD/PCDFs from street dust using PLE, with toluene as an alternative extraction solvent to those mentioned above.

When used as a PLE solvent, toluene is not often applied to the extraction of PCBs or other organic pollutants. However, for the determination of PCBs in sediments, Bandh et al. found that the use of PLE with toluene enabled better extraction efficiencies than PLE with hexane/acetone (1:1, v:v) or even Soxhlet extraction, depending on sulphur and carbon contents in the matrix [Bandh et al., 2000]. Toluene has been used for the extraction of PAH during the evaluation of a diesel particulate matter standard reference material, and comparability of PLE and Soxhlet was demonstrated [Schantz et al., 1997]. Toluene has also been used as a solvent to extract contaminated soil via PLE to determine levels of PCBs and PCDD/PCDFs. Contrary to the authors' expectations, toluene delivered unsatisfactory recoveries [Kiguchi et al., 2006].

In addition to the economic advantages of using PLE, the application of PLE enables environmental matrices to be extracted at elevated pressures and temperatures. This accelerates the kinetics of analyte desorption from the matrix. Richter et al. proposed that variation of the extraction temperature was the most effective optimization parameter [Richter et al., 1997]. The combined use of gas chromatography and mass spectrometry to separate and detect individual PCB congeners and the seventeen 2,3,7,8-chlorine substituted PCDD/PCDF congeners has been studied intensively in the recent decades [Ballschmiter and Zell, 1980; Ballschmiter et al., 1985; Focant et al., 2004].

The aim of this study is firstly to establish a simple and quantitative sampling technique for street dust. To our knowledge, this is the first investigation of mass transfer during sampling. Second, by the development of an efficient PLE method for the determination of PCBs and PCDD/PCDFs in street dust samples enables the evaluation of whether it is possible to use PLE with toluene as extraction solvent instead of more costly and time-consuming Soxhlet extraction method. Owing to the equivocal results found in the literature, the extraction temperature was optimized to achieve the highest extraction efficiency. The method's performance was checked by analysing NIST Standard Reference Material (SRM) 1649a for certified PCB congeners and reference values for PCDD/PCDF congeners. Finally, this study presents the first analysis of real street dust samples collected from industrial sites.

2.2 Materials and methods

2.2.1 Chemicals and materials

During development of the sampling and extraction methods, sea sand purchased from Merck (Darmstadt, Germany) was used as model matrix. The distributor reports that 90% of the sea-

sand particle size ranges in size from 100 to 300 µm. Toluene, n-hexane, dichloromethane, and n-decane were used for the extraction and clean-up step for residue analysis, and all were of picograde quality, purchased from LGC Promochem (Wesel, Germany). H_2SO_4, NaOH and $AgNO_3$ used during the clean-up were purchased from Merck and were at analysis quality. The $^{13}C_{12}$- and native PCB and PCDD/PCDF standards were purchased from Cambridge Isotopes Laboratories (Andover, USA). For the performance check of the analytical method, NIST Standard Reference Material (SRM) 1649a (Maryland, USA) was used. All PLE was performed using a Dionex ASE 200 system (Sunnyvale, USA).

2.2.2 Sampling technique

Quantitative sampling was tested on both concrete and asphalt surfaces that differed in surface roughness; i.e., the degree of unevenness elicited by gaps, holes, or channels in the surface. The asphalt ground corresponds more to real street sampling sites. Sea sand (1 g to 50 g) was homogeneously distributed over 1 m^2 of the respective surfaces after they had been cleaned with a broom and a hand brush. The size range of the particles of sea sand corresponds well to that of the collected material. Sampling was performed using a natural-bristle hand brush and a stainless steel scoop. The experiments were repeated five times, and the brushed sea sand was reweighed on a laboratory balance (accuracy ±0.01 g). The brush and the stainless steel scoop were thoroughly cleaned between experiments, and reused.

2.2.3 Temperature optimization for the PLE of PCBs and PCDD/PCDFs from street dust

To develop the PLE method, 1–2 g of sea sand was weighed into a glass fibre thimble (16 mm × 50 mm; Whatman Schleicher & Schuell, Dassel, Germany) and spiked with 100 µL of $^{13}C_{12}$-PCB quantification standard mixture. The glass fibre thimble filled with the spiked sea sand was placed into a 22-mL PLE extraction cell for the extractions. For extraction temperatures ranging from 100 °C to 160 °C, the recovery rates of the individual $^{13}C_{12}$-PCB quantification standards were determined. Toluene was chosen as PLE solvent, given its long-standing successful use as Soxhlet extraction solvent for the determination of PCBs and PCDD/PCDFs in several environmental matrices by our institute at LANUV NRW. Approximately 35 mL of toluene was required for PLE of each sample. The following extraction conditions were applied: extraction cycles, 1; extraction pressure, 110 bar; pre-heat time, 5 min; static extraction time, 5 min; flush volume, 60%; and purge time, 60 sec. After the extraction process, 5 mL of n-decane was added as keeper to the crude extract, and the

extract was subsequently concentrated to a 5-mL volume using a rotary evaporator. Before analysis and concentration via nitrogen flow to a final volume of 100 µL, $^{13}C_{12}$-2,2',3,3',4,4'-HexaCB (80 pg/µl; BZ #128) was added as a recovery standard. Concentration via nitrogen flow was performed between 80 and 90 °C. Therefore the extracts residue was transferred to a test tube and placed into a heating block. The analysis was performed in duplicate for each individual extraction temperature.

2.2.4 Soxhlet extraction

Soxhlet extraction was applied to a street dust sample to compare absolute recoveries for the $^{13}C_{12}$-PCB quantification standards with those obtained using PLE. Between 1 and 2 g of the dust sample was weighed into a glass fibre thimble (33 mm × 90 mm; Macherey-Nagel, Dueren, Germany), and extracted for at least 16 h. Approximately 300 mL of toluene was used for Soxhlet extraction. Prior to Soxhlet extraction, the dust sample was spiked with 100 µL of the $^{13}C_{12}$-PCB quantification standard mixture. As for the PLE procedure described above, 5 mL of n-decane was added as keeper to the crude extract, and the extract was subsequently concentrated to a 5-mL volume using a rotary evaporator. Subsequently, the clean-up step described below was applied to the crude sample extracts. The recovery standard $^{13}C_{12}$-2,2',3,3',4,4'-HexaCB (80 pg/µl; BZ #128) was added before concentration to a final volume of approximately 100 µL via nitrogen flow and analysis. Using isotope dilution analysis for the quantification of PCBs and PCDD/PCDFs the samples final volume plays only a minor role.

2.2.5 Simultaneous extraction of PCDD/PCDFs from street dust sample

As mentioned above, the primary aim of this study was to analyse PCB levels. However, extraction and determination of PCDD/PCDF levels in street dust samples were performed simultaneously. Therefore, NIST SRM 1649a and a real dust sample were spiked additionally with 100 µL of a $^{13}C_{12}$-PCDD/PCDF quantification standard mixture. Samples were extracted using PLE under the same conditions as those described above. The clean-up step described below was applied to the crude sample extract. After adding 100 µL $^{13}C_{12}$-1,2,3,4-TCDD and $^{13}C_{12}$-1,2,3,7,8,9-HxCDD recovery standard solution (4.0 pg/µl), samples were concentrated via nitrogen flow to a final volume of approximately 10 µL for the PCDD/PCDF fraction, and then analysed. Standard concentrations are shown in the Supporting Information section.

2.2.6 Clean-Up procedure

Except for the development of the extraction method, which involved spiked sea sand, all sample extracts were subjected to a clean-up procedure to eliminate interfering co-extracted matrix components from the crude sample extract. These matrix components may adversely affect analysis by causing peak tailing or fronting, peak broadening, co-elution, or the formation of ghost peaks. The clean-up procedure consisted of two steps. In accordance with EN 1948-2 [EN 1848-2, 2006], multi-layer solid phase chromatography with silica modified with either 44% H_2SO_4, 33% NaOH or 10 % $AgNO_3$ was applied as the primary clean-up step. A solid-phase chromatography column (30 mm × 300 mm) was filled in the following order: 2 g silica, 1 g $AgNO_3$/silica, 2 g silica, 5 g NaOH/silica, 2 g silica, 10 g H_2SO_4/silica, 2 g silica, and 10 g sodium sulphate. The filled chromatography column was pre-washed with 300 mL n-hexane before the sample was applied to this column, and the sample was then eluted following addition of another 300 mL of n-hexane.

The eluate, concentrated to a volume of 5 mL via rotary evaporation, was subsequently applied to a basic alumina column (MP Alumina B – Super I, MP Biomedicals, Eschwege, Germany) for the separation of PCBs and PCDD/PCDFs. To this end, 25 g alumina was slurry packed into a chromatography column (24 mm × 300 mm) filled with n-hexane. Sodium sulphate (10 g) was added to the top of the alumina layer. After n-hexane had drained off, the sample solved in n-decane was added to this column. A 60-mL fraction of n-hexane was discarded before the PCB fraction was eluted with 80 mL of toluene. The PCDD/PCDF fraction was eluted using 200 mL 1:1 (v/v) n-hexane/dichloromethane. Finally, each fraction was concentrated via nitrogen flow as described above.

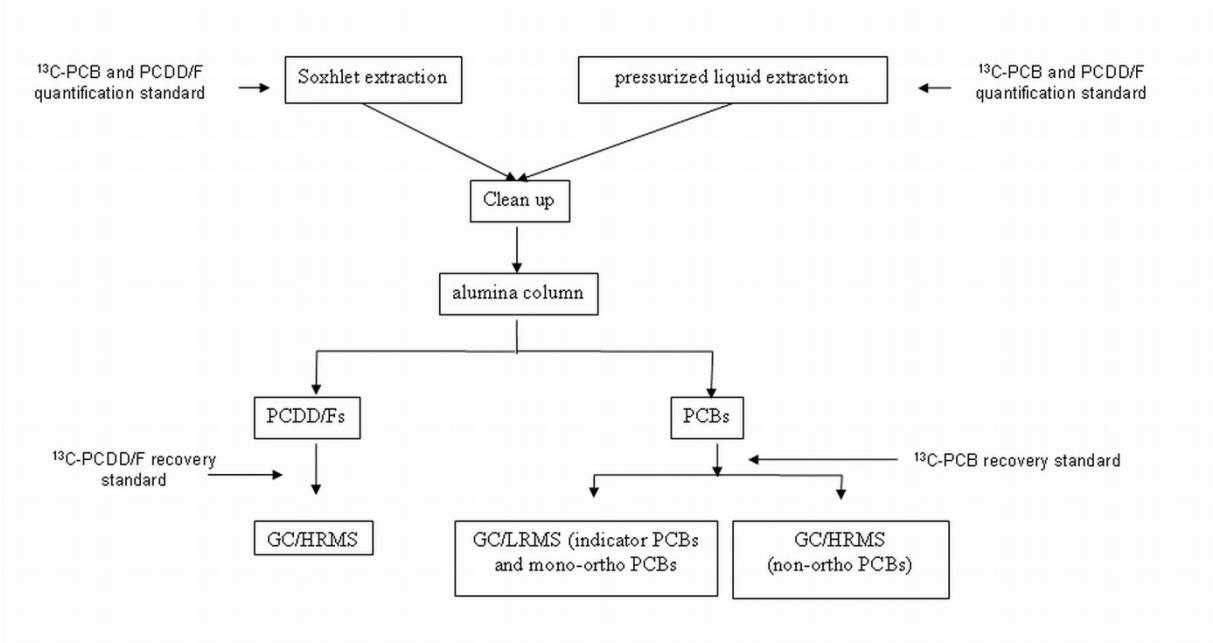


Figure 4 Analytical scheme for the determination of PCBs and PCDD/PCDFs in street dust samples.

2.2.7 Chromatographic analysis

2.2.7.1 Analyis of PCBs

In accordance with DIN EN 1948-4 [EN 1948-4, 2006] a gas chromatography instrument (GC; model 6890N with an autosampler model 7683) and a low resolution mass spectrometer (model 5973N) (all Agilent, Santa Clara, USA) were used for the analysis of the indicator PCBs #28, #52, #101, #138, #153, #180 and the dioxin-like PCB congeners #123, #118, #114, #105, #167, #156, #157, #189. Total PCB levels were calculated according to EN 12766-2 [Petroleum products and used oils, 2001] by multiplying the sum of the six indicator PCB mass concentrations by five. Helium 5.0 was used as carrier gas at a constant flow rate (1.0 mL min-1). The GC was equipped with a DB-5 column (J&W Scientific, Folsom, USA) (50 m; 0.20 mm I.D.; 0.11 µm film thickness). Electron impact was used for ionization, and electron energy was set to 70 eV. The column oven temperature program was started at 120 °C, held at 120 °C for 1 min, heated to 220 °C at a rate of 15 °C/min, heated to 230 °C at a rate of 1.50 °C/min, and then heated to 300 °C at a rate of 15 °C/min. The final temperature of 300 °C was held for 10 min. The splitless injection temperature was maintained at 250 °C, and the ion-source temperature was maintained at 280 °C. A sample volume of 1 µL was injected. Recorded qualification and quantification mass-to-charge ratios (m/z) are summarized in the Supporting Information.

The mono-ortho PCB congeners #77, #81, #126, #169 were analysed using a GC model 6890 Series 2 (Agilent) with a CTC HTX PalPlus autosampler and a high-resolution mass spectrometer (model DFS; Thermo Fisher Scientific, Bremen, Germany). The GC was equipped with a DB-5 column (J&W) (50 m; 0.20 mm I.D.; 0.11 µm film thickness). Helium 5.0 was used as carrier gas at a constant flow rate of 1.0 mL/min. Starting at 100 °C (maintained for 1.5 min), the temperature was increased first to 180 °C at a rate of 20°C/min, then to 260 °C at a rate of 2 °C/min, and finally to 300 °C at a rate of 4 °C/min. This temperature was held for another 4 min. Splitless injection (1 µL) was performed at 250 °C, and the ion-source temperature was set to 260 °C. Electron impact was used for ionization, and electron energy was set to 44 eV. For all measurements mass spectrometric resolution was set to 10'000. Quantification of PCB congeners and PCB homologues in street dust was performed using isotope dilution analysis.

2.2.7.2 Analysis of PCDD/PCDFs

Analysis for all 2,3,7,8-PCDD/PCDF and PCDD/PCDF homologue groups, starting with tetrachloro homologues, was performed in accordance with DIN EN 1948-2 [EN 1948-2, 2006] and DIN EN 1948-3 [EN 1948-3, 2006] on a GC model 6890 Series 2 (Agilent) with a CTC HTX PalPlus autosampler (CTC Analytics, Zwingen, Switzerland) and a high resolution mass spectrometer model DFS (Thermo Fisher Scientific). The GC was equipped with a SP-2331 column (Supelco, Bellefonte, USA) (60 m; 0.25 mm I.D.; 0.20 µm film thickness). Helium 5.0 was used as the carrier gas at a constant flow rate of 1.0 mL/min. Starting at 120 °C and holding this temperature for 2 min, the GC column oven was heated to 220 °C at a rate of 30 °C/min, before the final temperature of 260 °C was achieved by increasing the temperature at a rate of 1.20 °C/min. The temperature was held at 260 °C for a further 18 min. Splitless injection (1 µL) was used at a temperature of 250 °C and the ion-source temperature was set to 260 °C. Electron impact was used for ionization, and the electron energy was set to 44 eV. Recorded qualification and quantification mass-to-charge ratios m/z are summarised in the Supporting Information. For all measurements, mass spectrometric resolution was set to 10'000. As calibration compound FC5311 (MasCom, Bremen, Germany) at m/z 316.9824 for tuning, optimization and resolution adjustment was used. Quantification of PCDD/PCDF congeners and PCDD/PCDF homologues in street dust was performed by isotope dilution analysis.

2.2.8 Quality assurance

Quality control for the analysis of PCBs and PCDD/PCDFs was carried out in accordance with DIN EN 1948 3-4 [EN 1948-3 and EN 1948-4, 2006]. After comparison of the retention time between native and ^{13}C-labelled analytes, relative isotope ratios were considered with a tolerance of 20% for peak identification. Limits of detection (LOD) were established to be three times the baseline noise, and limits of quantification (LOQ) were defined as ten times the baseline noise. To monitor the method's overall performance, the standard recoveries were checked. A five-point calibration was performed, which was checked for variation at least once every 14 days by measuring a calibration standard with a defined concentration level. Quantification for the individual PCB and PCDD/PCDF congeners was based on daily generated response factors that were calibrated against the relevant $^{13}C_{12}$-labeled quantification standard. Exceptions are 1,2,3,7,8,9-HxCDD (which was related to 1,2,3,6,7,8-HxCDD), 1,2,3,7,8-PeCDF (which was related to 2,3,4,7,8-PeCDF), 1,2,3,7,8,9-HxCDF (which was related to 2,3,4,6,7,8-HxCDF), and 1,2,3,4,7,8,9-HpCDF (which was related to 1,2,3,4,6,7,8-HpCDF). As validation criterion for the response factors the approach introduced in EN 1948-3 was adapted for this study. In EN 1948-3 it is proposed that the calibration and also the generated response factors are valid as long as a deviation under 20% for a single calibration is determined [EN 1948-3, 2006]. Furthermore, precision and accuracy were checked by analysing the NIST Standard Reference Material (SRM) 1649a. This street dust reference sample is certified for PCB analysis, and reference values are provided for PCDD/PCDF analysis.

2.3 Results and discussion

2.3.1 Determination of the effectiveness of sampling

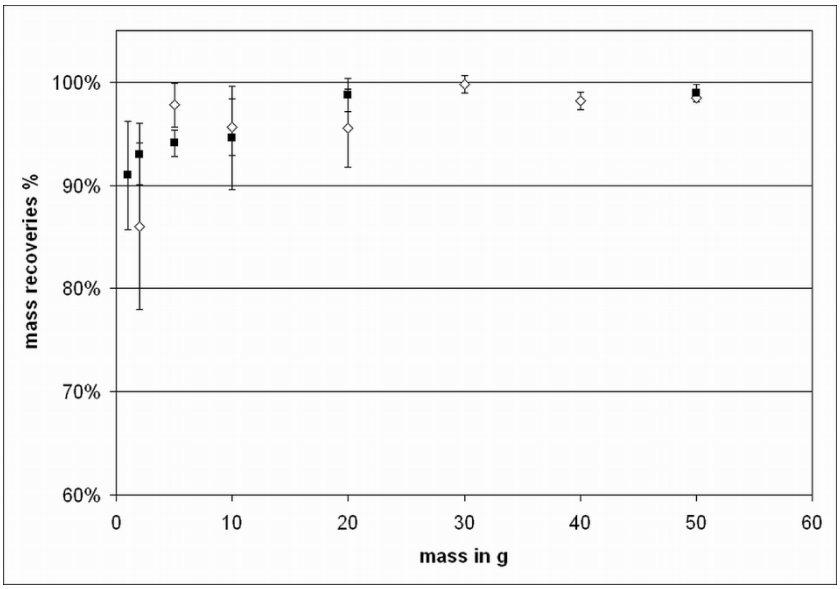


Figure 5 Average percentage mass recoveries (n = 5) with the corresponding standard deviations associated with different masses of spiked sea sand on a concrete surface (filled squares) and on an asphalt surface (open diamonds).

Mass recoveries of applied sea sand on a concrete and asphalt surface are shown in **Figure 5**. According to the distributor, 90% of the sand particles range in size from 100 to 300 µm, making this a good surrogate for real street dust. This experiment demonstrated that the recovery rates of the sample mass were in general greater than 90%, with the exception of one low sample mass (2 g) on an asphalt surface (recovery rate 86%). For mass loads larger than 20 g, the sampling efficiency approached 100% (**Figure 5**). In general, for lower mass loads, higher mass recoveries were found on a concrete surface than on an asphalt surface. Even small sample masses (about 1 g) can be recovered from concrete surfaces with an efficiency of greater than 90%, whereas small masses (less than 2 g) can only be recovered from asphalt surfaces with an efficiency of approximately 85%. The determined standard deviations for the mass recoveries on both surfaces, for small sampling masses, correlate closely with the roughness of the surface. Depending on the recovery rate that is regarded as sufficient for quantitative sampling, it is not advisable to sample street dust masses less than 5 g.

2.3.2 Pressurized liquid extraction of PCB and PCDD/PCDF from street dust

2.3.2.1 Variation of the extraction temperature in PLE for the extraction of PCBs from the model matrix

As mentioned above, extraction temperature and the choice of extraction solvent are the most effective optimization parameters for PLE [Richter et al., 2006; Ramos et al., 2002]. To study the influence of extraction temperature on the extraction efficiency of PCB from the model matrix, the recovery rates of the $^{13}C_{12}$-PCB quantification standards were calculated after PLE at extraction temperatures of 100 °C, 120 °C, 140 °C and 160 °C. The recovery rates of the individual $^{13}C_{12}$ PCB quantification standards for various extraction temperatures are shown in **Figure 6**.

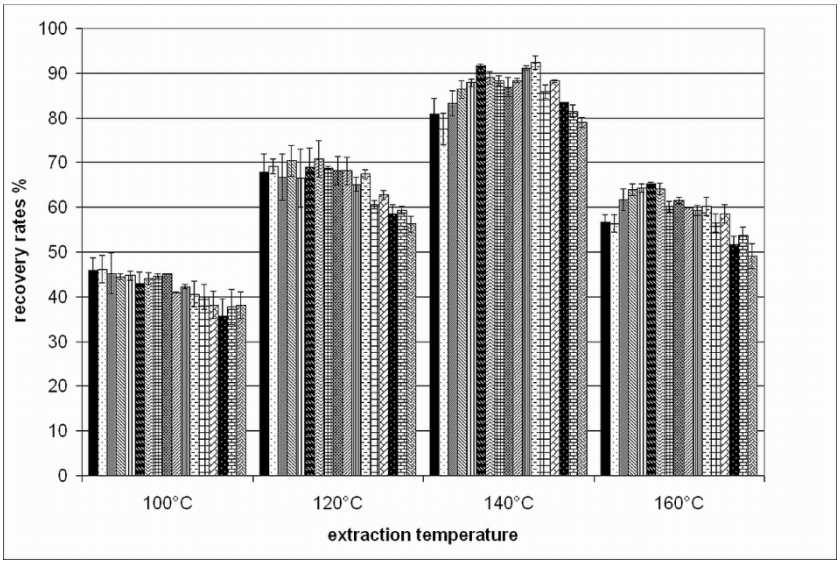


Figure 6 Average percentage recovery rates of $^{13}C_{12}$-PCB quantification standards (from left to right: #28, #52, #101, #123, #118, #114, #153, #138, #167, #156, #157, #180, #189, #194, #208, #209) at different PLE extraction temperatures. The determination was performed in duplicate.

An extraction temperature of 140 °C delivers the best recovery rates for the extraction of PCB from the model matrix. The recovery rates range from 78% (for $^{13}C_{12}$-2,2',5,5'-TetraCB) to 92% (for $^{13}C_{12}$-2,3,3',4,4',5'-HexaCB). As shown in **Figure 6**, the extraction of the model matrix at a PLE extraction temperature of 140 °C results in homogenous recovery rates for poorly chlorinated PCB (tetrachlorinated biphenyl) as well as for the most chlorinated PCB (decachlorinated biphenyl). Furthermore, as shown in **Figure 6**, the reproducibility of the

extraction at an extraction temperature of 140 °C was very good, with an average range of the recovery rates for all congeners of 1.3% (in duplicate measurements). All other extraction temperatures tested provided higher deviations in duplicate measurements for all congeners. An increased extraction temperature of 160 °C did not improve recovery rates of the $^{13}C_{12}$-PCB quantification standards. Similar observations have already been reported for thermolabile compounds after increasing the extraction temperature [Björklund and Nilsson, 2000]. However, persistent organic pollutants cannot be regarded as thermolabile substances. A previous investigation of the PLE extraction temperature needed to extract PCBs and PCDD/PCDFs from contaminated soil reported that an increase in extraction temperature from 150 °C to 175 °C or 200 °C delivered slightly lower recovery rates than PLE at 150 °C for dioxin-like and non-ortho PCBs [Kiguchi et al., 2007]. The results of the extraction temperature optimization here agree well with these observations, although the mechanism underlying this phenomenon remains unknown. Furthermore, a consecutive complete second–step extraction was performed and did not lead to a quantifiable improvement of the extraction efficiency. Optimization of the extraction pressure during PLE method development has been neglected due to the consistent finding in literature that extraction pressure only plays a minor role for the extraction efficiency [Ramos et al., 2002].

2.3.2.2 Determination of PCB in NIST SRM 1649a

The concentrations of 29 PCB congeners in NIST SRM 1649a are certified. The so-called indicator PCBs (#28, #52, #101, #138, #153, #180) and in addition three dioxin-like PCBs (#105, #118, #156) were used to compare the experimentally determined concentrations with the certified concentrations. The six indicator congeners play a major role in the estimation of total PCB in almost all environmental samples. Multiplication of the concentrations of the six indicator PCBs by the empirical factor 5 is used to estimate total PCB concentrations (total PCBs) [Petroleum products and used oils, 2001]. This approach is used, for example, in regulation EC 850/2004, where a threshold value for PCB in waste is prescribed [Regulation 850/2004/EC, 2004]. Furthermore, this threshold value was used as a comparative parameter for analysed PCB burdens of dusts from industrial premises in a governmental research program underlining the major concern of those congeners in street dusts [Schwerpunktinspektionsprogramm PCB, 2012]. The determination of PCBs in the SRM was performed in four individual analyses. After extraction via PLE using the conditions established in this work, the clean-up step mentioned above was applied to the extract. A comparison of the certified concentrations (including expanded confidence intervals) with

concentrations determined (including expanded confidence intervals) using the PLE-based method described here is shown in **Figure 7**. The analysed concentrations of the six indicator PCBs are within the confidence intervals certified by NIST, except for congener #52. Thus, with this one exception, our analysis demonstrated accurate determination of PCB levels in urban dust. Regarding the determination of the three dioxin-like PCBs unsatisfactory results have been achieved. Only the analysed concentration of #118 is within the confidence interval certified by NIST. For #105 and #156 the analysed concentrations are outside the confidence intervals reported by NIST. Especially for #105 a possible co-elution on a 5%-(phenyl)-methylpolysiloxan stationary phase with #127 can explain the overestimation during analysis, as indicated in EN 1948-4 [EN 1948-4, 2010]. By extrapolating the results of the accuracy parameters established for the three analyzed dioxin-like PCBs to the ones not certified by NIST, the subsequent calculation of the toxicity equivalent (TEQ) for PCBs has to be regarded as an albeit small source of error. To evaluate PLE in the extraction of PCBs in SRM 1649a, Schantz et al. used hexane/acetone acetonitrile and dichloromethane as PLE extraction agent. Furthermore, Soxhlet extraction was used for the certification of PCB in SRM 1649a, in an independent analysis [Schantz et al., 1997]. The results after Soxhlet and PLE were used for the calculation of the certified concentration values in SRM 1649a. The use of toluene for extraction generated comparable values for established concentrations of the reference material sample.

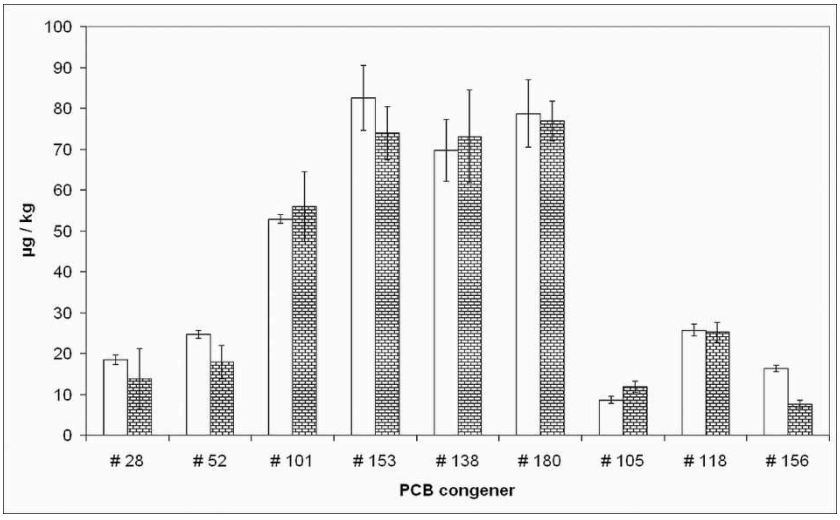


Figure 7 Analysis of NIST SRM 1649a and comparison of experimentally determined average concentrations (masoned bars) with the certified concentrations (white bars). Certified analysis confidence intervals and ranges determined in this study are shown. The determination was performed in duplicate.

2.3.2.3 Comparison of Soxhlet and PLE for the extraction of a street dust sample

Aliquots of a street dust sample were concurrently extracted with both standard Soxhlet method and the PLE approach described above. The clean-up step described above was then applied to the crude extracts. Both extracts were treated identically for the estimation of extraction efficiencies. Recovery rates for the individual $^{13}C_{12}$-PCB quantification standards are shown in **Figure 8**. It can be inferred that PLE provides higher recovery rates for all congeners than classical Soxhlet extraction. Recovery rates using PLE were 52%–77%. In contrast, Soxhlet extraction produces lower recovery rates of 37%–52%. Bandh et al. reported recovery rates for $^{13}C_{12}$-standards added prior to Soxhlet and PLE extraction, which ranged from 67% to 97% in sediments [Bandh et al., 2000]. In their study, the clean-up applied to the extracts was similar complex to that of the present study. For the extraction of contaminated soil samples, Kiguchi et al. reported that recovery rates for $^{13}C_{12}$-standards added prior to the clean-up of the extracts ranged from 62% to 120% [Kiguchi et al., 2006]. For Soxhlet extraction and PLE using toluene as extraction agent good recovery rates for the individual $^{13}C_{12}$-PCDD/PCDF quantification standard were achieved. For both substance classes higher recovery rates for the $^{13}C_{12}$-quantification standards were obtained by using PLE. Absolute recovery rates for these standards ranges between 81 and 112% for Soxhlet extraction and 96 and 121% for PLE, respectively. Detailed information of congener specific recovery rates is given in the Supplementary Information. The difference in recovery rates of PCBs and PCDD/PCDFs for the PLE of street dust samples suggests that PCBs are more tightly bound to the matrix than PCDD/PCDFs [Kiguchi et al., 2006].

Comparing the recovery rates of the $^{13}C_{12}$-PCB quantification standards added prior to the extractions in this study with these results reported by others, the results obtained during PLE extraction testify to the efficacy of the extraction method developed in this study. Comparison of how the absolute recovery rates of the $^{13}C_{12}$-PCB quantification standards during the PLE extraction temperature vary for spiked sea sand (**Figure 8**), compared with the rates determined for real street dust after applying the crude sample extract to the clean-up step, suggests partial loss of quantification standards during the clean-up. The clean-up approach includes several evaporation processes that should lead to a greater loss of poorly chlorinated compounds owing to their higher vapour pressure. In addition, the variability in duplicate measurements for Soxhlet extraction is relatively high, compared with that for PLE. Similar findings for Soxhlet extraction have been reported by Kiguchi et al., who therefore proposed

an additional extraction step to ensure satisfactory extraction [Kiguchi et al., 2006] and demonstrated this successfully for PLE in a subsequent survey [Kiguchi et al., 2007]. However, the results reported by Kiguchi et al. regarding the efficiency of extraction of PCB from forest soil after PLE with toluene are not consistent with the results presented in the present work.

According to Kiguchi et al., Soxhlet extraction with toluene showed better extraction yields than single-step PLE, and the extraction process seemed to be incomplete after a single-step PLE [Kiguchi et al., 2006]. Also, the results obtained in the study by Bandh et al., where toluene was used for the PLE of sediments at 160 °C, delivered lower recoveries using PLE than Soxhlet [Bandh et al., 2000], which is opposite to the present results. The present study demonstrates that PLE offers an attractive alternative to Soxhlet extraction for the analysis of street dust samples. In Soxhlet extraction, approximately 300 mL of toluene per sample is used for a time-consuming extraction step that lasts at least 18 h. In contrast, use of PLE requires approximately only one-tenth as much extraction solvent per sample of street dust, and the entire extraction cycle can be completed within 30 min. This underlines the benefits of using PLE as the extraction method of choice for the analysis of street dust.

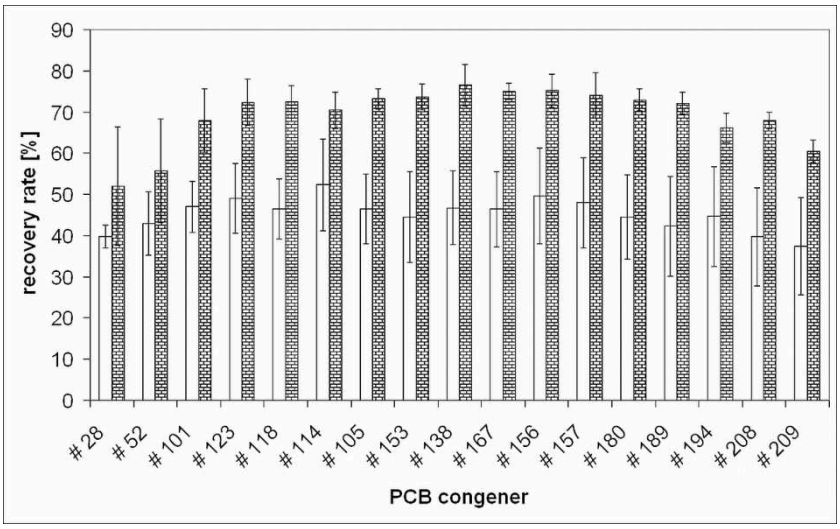


Figure 8 Comparison of the recovery rates of the $^{13}C_{12}$-PCB quantification standards for a street dust sample after Soxhlet (white bars) and PLE (masoned bars). All extracts were cleaned up using the procedure introduced in this study. The ranges (n = 2) for each extraction technique are given as error bars.

2.3.2.4 Determination of PCDD/PCDF levels in NIST SRM 1649a

Reference concentrations of all seventeen 2,3,7,8-chlorine substituted PCDD/PCDF congeners are given in NIST SRM 1649a. Furthermore, reference homologue levels and the toxicity equivalent (TE) of PCDD and PCDF are known. A crossplot of reference and analysed concentrations of NIST SRM 1649a is shown in **Figure 9**.

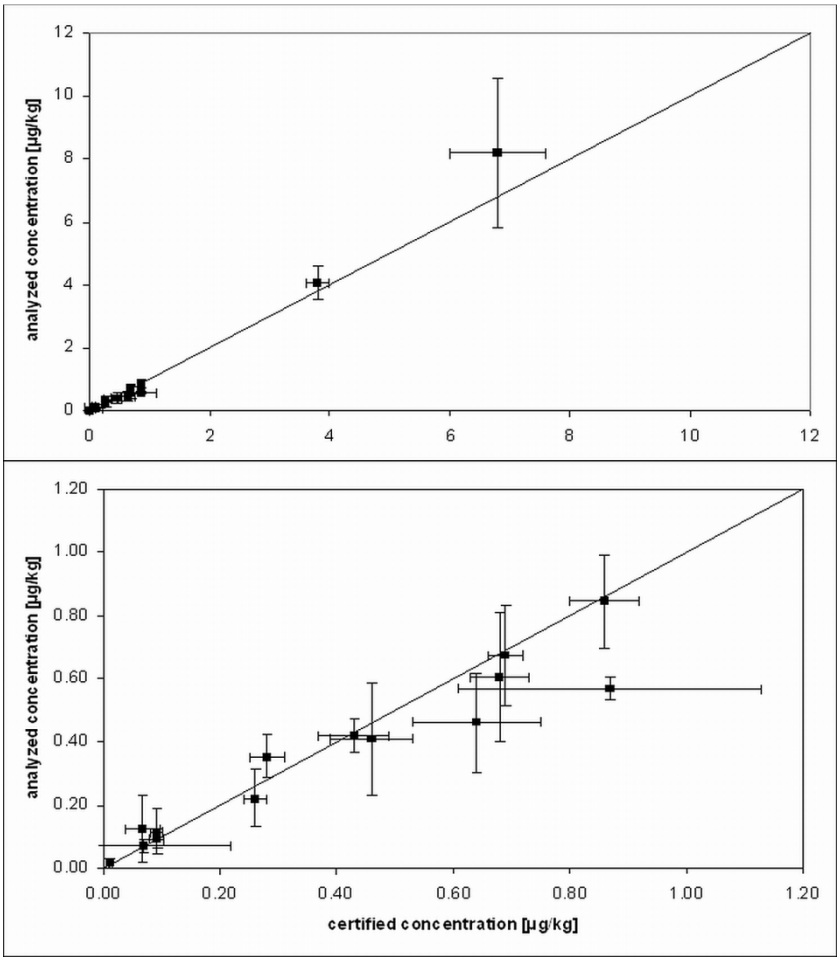


Figure 9 Comparison of reference concentrations of the 17 PCDD/PCDF congeners with the experimentally determined average concentrations (upper figure). The results for lower concentrations are enlarged in the lower figure. Reference intervals (x-axis) and measured ranges (y-axis) are also shown. The diagonal 1:1 line indicates a perfect match of concentrations. The determination was performed in duplicate.

Table 6 NIST reference values for the tetra- to heptachlorodibenzodioxin and from tetra- to heptachlorodibenzofurane homologue groups and their 95% confidence interval in NIST1649a and concentrations and their 95% confidence interval (n=4) determined in this work.

	NIST 1649a	
	reference concentration	Analyzed concentration
	µg/kg	µg/kg
Total TCDD	0.16 ± 0.08	0.23 ± 0.055
Total PeCDD	0.88 ± 0.16	1.3 ± 0.17
Total HxCDD	6.0 ± 0.5	6.9 ± 0.45
Total HpCDD	36.4 ± 3.4	37 ± 4.4
Total TCDF	0.52 ± 0.13	1.0 ± 0.34
Total PeCDF	1.6 ± 0.2	2.8 ± 0.87
Total HxCDF	5.0 ± 0.6	5.8 ± 1.0
Total HpCDF	9.8 ± 0.8	9.6 ± 2.0

As reported for the determination of PCB levels in street dust samples, the accuracy for the PCDD/PCDF determination is satisfactory. Almost all analysed 2,3,7,8-chlorine substituted PCDD/PCDF congeners match the reference concentrations established by NIST. Exceptions are observed for 1,2,3,7,8,9-HxCDD, 2,3,4,7,8-PeCDF and 1,2,3,4,7,8-HxCDF. Here, the analysed concentrations and confidence intervals do not fit into the confidence intervals provided by NIST analyses. The expanded uncertainties expressed as 95% confidence interval from the quadruplicate determination of each analysed PCDD/PCDF congener and homologue in SRM 1649a was used for the comparison with 95% confidence intervals provided by NIST. The determined TEQ in the present study is 0.85 ± 0.15 µg/kg. The NIST certificate for SRM 1649a provides a value for the TEQ of 0.86 ± 0.06 µg/kg. Despite the minor variations between analysed and reference concentration of the individual 2,3,7,8-chlorine substituted PCDD/PCDF congeners in SRM 1649a the determination of PCDD/PCDFs and their toxicity potential in street dust can be regarded as satisfactory for the purpose of this study. A comparable result is obtained for the determination of PCDD/PCDF homologues. As can be seen in

Table 6, only the analysed ranges for total PeCDD and HxCDD do not match the reference values by NIST. In this study, a homologue group is considered to be identified as one peak. This means that the area defined by one homologue group gets integrated for the certain homologue group in accordance to the recorded m/z and the retention time window. During an inter-laboratory study for the evaluation process of the 2,3,7,8-chlorine substituted PCDD/PCDFs and the homologue groups in SRM 1649a, the participants used their own routine analytical procedures [Chiu et al., 2001]. Consequently, the method of determination of the homologue groups cannot be readily deduced from the literature.

2.3.3 Application to real street dust samples for the determination of PCBs and PCDD/PCDFs

The described method was applied to real street dust samples (n = 22) collected from industrial sites. Here we present the results of investigations of the median particle sizes and the PCB and PCDD/PCDF loads of dust samples. Median particle diameters were 250–500 µm. Compared with the particle sizes of the sea sand used for the evaluation of the sampling technique, the median diameters of the sample particles are much larger. Thus, the choice of sea sand as a surrogate seems justified. The application of this sampling technique helped to detect with little effort the contamination distribution based on improper handling of PCB laden condensers and transformers. At this contaminated site, total PCB concentrations as high as 48,000 mg/kg were detected. The overall range of total PCB concentrations in industrial street dust samples ranged from 2 to 48,000 mg/kg and the PCDD/PCDF TEQ concentrations ranged from 0.0055 to 55 µg TEQ/kg [Bruckmann et al., 2011]. Owing to the relatively high concentration of PCB and PCDD/PCDF in street dust, a more extensive study is underway to determine the concentrations of PCBs and PCDD/PCDFs in various samples. In addition, more detailed investigations with regard to sampling site categories (background, urban, urban with industrial influence, industrial) are ongoing.

2.4 Conclusion

A method for quantitative sampling of street dust is presented. Differences in mass recovery between two surfaces with different roughnesses were observed for low dust loads. Quantitative sampling of street dust enables the determination of the total deposition load by measuring the initial mass of the street dust and the sampling area. The use of PLE of street dust samples provides a powerful alternative to classical Soxhlet extraction. It has been shown that the use of toluene for the extraction of PCBs and PCDD/PCDFs enables satisfactory

recovery rates and experimentally determined concentrations that are comparable to certified (PCBs) and reference (PCDD/PCDFs) values.

2.5 References

Ballschmiter, K.; Zell, M. Analysis of polychlorinated biphenyls (PCB) by glass capillary gas chromatography. Fres. J. Anal. Chem. 1980, 302, 20-31.

Ballschmitter, K.; Buchert, H.; Class, T.; Krämer, W.; Magg, H.; Munder, A.; Reuter, U.; Schäfer, W.; Swerev, M.; Wittlinger, R. Isomerenspezifische Bestimmung der Polychlordibenzodioxine (PCDD) und Polychlordibenzofurane (PCDF). Fresenius J. Anal. Chem. 1985, 320, 711-717.

Bandh, C.; Björklund, E.; Mathiasson, L.; Näf, C.; Zebühr, Y. Comparison of Accelerated Solvent Extraction and Soxhlet Extraction for the Determination of PCBs in Baltic Sea Sediments. Environ. Sci. Technol. 2000, 34, 4995-5000.

Björklund, E.; Bøwadt, S.; Nilsson, T.; Mathiasson, L. Pressurized fluid extraction of polychlorinated biphenyls in solid environmental samples. J. of Chromatogr. A 1999, 836, 285-293.

Björklund, E.; Nilsson, T. Pressurised liquid extraction of persistent organic pollutants in environmental analysis. Trends in Anal. Chem. 2000, 19, 434-445.

Bruckmann, P.; Hiester, E.; Klees, M.; Radermacher, L. Environmental pollution by polychlorinated biphenyls (PCB) in the harbour region of Dortmund. Gefahrst. Reinhalt. der Luft 2011, 4, 151-158.

Chiu, C.; Turle, R.; Poole, G.; Thibert, B.; Brubaker jr., W.; Schantz, M.; Wise, S. Determination of polychlorinated dibenzo-p-dioxin and dibenzofuran congeners in air particulate and marine sediment standard reference materials (SRMs). Fresenius J. Anal. Chem. 2001, 369, 356-363.

de Miguel, E.; Llames, J.F.; Chacón, E.; Berg, T.; Larssen, S.; Røyset, O.; Vadset, M. Origin and patterns of distribution of trace elements in street dust: Unleaded petrol and urban lead. Atmos. Environ. 1997, 31, 2733-2740.

Focant, J.F.; Reiner, E.J.; MacPherson, K.; Kolic, T.; Sjödin, A.; Patterson jr., D.G.; Reese, S.L; Dorman, F.L.; Cochran, J. Measurement of PCDDs, PCDFs, and non-ortho-PCBs by

comprehensive two-dimensional gas chromatography-isotope dilution time-of-flight mass spectrometry (GC x GC-IDTOFMS). Talanta 2004, 63, 1231-1240.

Harrad, S.; Hazrati, S.; Ibarra, C. Concentrations of Polychlorinated Biphenyls in Indoor Air and Polybrominated Diphenyl Ethers in Indoor Air and Dust in Birmingham, United Kingdom: Implications for Human Exposure. Environ. Sci. Technol. 2006, 40, 4633-4638.

Irvine, K.N.; Loganathan, B.G. Localized enrichment of PCB levels in street dust due to redistribution by wind. Water, Air and Soil Pollution 1998, 105, 603–615.

Kiguchi, O.; Kobayashi, T.; Saitoh, K. Pressurized liquid extraction of polychlorinated dibenzo-p dioxins, polychlorinated dibenzofurans and coplanar polychlorinated biphenyls from contaminated soil. J. of Chromatogr. A 2006, 1108, 176-182.

Kiguchi, O.; Saitoh, K.; Ogawa, N. Simultaneous extraction of polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans and coplanar polychlorinated biphenyls from contaminated soil using pressurized liquid extraction. J. of Chromatogr. A 2007, 1144, 262-268.

National Institute of Standards and Technology (2007) Certificate of Analysis; Standard Reference Material 1649a Urban Dust

Petroleum products and used oils .Determination of PCBs and related products. Part 2: Calculation of polychlorinated biphenyl (PCB) content; German version EN 12766-2:2001

Poster, P.; Schantz, M.; Wise, S.; Vangel, M. Analysis of urban particulate standard reference materials for the determination of chlorinated organic contaminants and additional chemical and physical propertiesFresenius J. Anal. Chem. 1999, 363, 380-390.

Ramos, L.; Kristenson, E.M.; Brinkman, U.A.Th. Current use of pressurised liquid extraction and subcritical water extraction in environmental analysis. J. of Chromatog. A 2002, 975, 3-29.

Regulation 850/2004/EC of the European parliament and board dealing with persistent organic pollutants, 30.04.2004, L 158

Richter, B.E.;Ezzell, J.L.; Knowles, D.E.; Hoefler, F.; Mattulat, A.K.R.; Scheutwinkel, M.; Waddell, D.S.; Gobran, T.; Khurana, V. Extraction of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans from environmental samples using accelerated solvent extraction (ASE). Chemosphere 1997, 34, 975-987.

Schantz, M.; Nichols, J.J.; Wise, S. Evaluation of Pressurized Fluid Extraction for the Extraction of Environmental Matrix Reference Materials. Anal. Chem. 1997, 69, 4210-4219.

Schwerpunktinspektionsprogramm PCB. Inspektion von Anlagen, in denen PCB-haltiger-Abfall anfällt oder entsorgt wird. LANUV-Fachbericht 39. ISSN 1864-3930 LANUV-Fachberichte. 2012.

Stationary source emissions – Determination of the mass concentration of PCDDs/PCDFs and dioxin-like PCBs – Part 2: Extraction and clean-up of PCDDs/PCDFs; German version EN 1948-2:2006

Stationary source emissions – Determination of the mass concentration of PCDDs/PCDFs and dioxin-like PCBs – Part 3: Identification and quantification of PCDDs/PCDFs; German version EN 1948-3:2006

Stationary source emissions – Determination of the mass concentration of PCDDs/PCDFs and dioxin-like PCBs – Part 4: Sampling and analysis of dioxin-like PCBs; German version EN 1948-4:2010

Takada, H.; Onda, T.; Harada, M.; Ogura, M. Distribution and sources of polycyclic aromatic hydrocarbons (PAHs) in street dust from the Tokyo Metropolitan area. Sci. Total Environ. 1991, 107, 45-69.

Yang, Y.; Baumann, W. Study of polychlorinated biphenyls in street dust by supercritical fluid extraction gas chromatography/mass spectrometry. Fresenius J. Anal. Chem. 1996, 354, 56-60.

Zhang, Z.; Ohiozebau, E.; Rhind, S. Simultaneous extraction and clean-up of polybrominated diphenyl ethers and polychlorinated biphenyls from sheep liver tissue by selective pressurized liquid extraction and analysis by gas chromatography–mass spectrometry. J. of Chromatogr. A 2011, 1218, 1203-1209.

2.6 Supporting Information

Table S 1 Single mass recorveries for sea sand on concrete and asphalt ground. Additionally the average of a five time determination and the standard deviation is calculated. The amount of spiked sea sand can be found in the headline.

		1g	2g	5g	10g	20g	30g	40	50g
Concrete ground	1	89,1%	90,5%	94,2%	96,8%	96,4%	-	-	98,2%
	2	98,0%	92,5%	94,8%	90,6%	100,8%	-	-	100,2%
	3	94,1%	91,0%	94,6%	95,2%	98,8%	-	-	98,5%
	4	84,2%	93,0%	95,0%	88,9%	99,3%	-	-	98,4%
	5	89,5%	98,0%	91,8%	101,4%	98,6%	-	-	99,4%
	average	91,0%	93,0%	94,1%	94,6%	98,8%	-	-	98,9%
	Standard deviation	±5,3%	±3,0%	±1,3%	±5,0%	±1,6%	-	-	±0,8%
Asphalt ground	1	-	73,7%	97,0%	94,7%	98,9%	101,3%	99,0%	96,9%
	2	-	95,1%	100,4%	98,0%	92,4%	99,5%	99,2%	97,3%
	3	-	86,1%	97,4%	95,3%	94,2%	99,2%	98,1%	100,1%
	4	-	91,0%	99,2%	91,8%	100,2%	99,7%	97,1%	99,2%
	5	-	84,3%	94,9%	98,4%	92,1%	99,5%	97,8%	98,8%
	average	-	86,0%	97,8%	95,7%	95,6%	99,8%	98,2%	98,5%
	Standard deviation	-	±8,1%	±2,1%	±2,7%	±3,8%	±0,83%	±0,85%	±1,4%

Table S 2 Composition of the $^{13}C_{12}$-PCB quantification standard mixture

$^{13}C_{12}$-PCB quantification standard	PCB #	concentration [pg/µL]
$^{13}C_{12}$ - 2.4.4'-TriCB	28	80.0
$^{13}C_{12}$ - 2.2'.5.5'-TetraCB	52	78.8
$^{13}C_{12}$ - 3.4.4'.5 - TetraCB	81	19.9
$^{13}C_{12}$ - 3.3'.4.4'-TetraCB	77	19.9
$^{13}C_{12}$ - 2.2'.4.5.5' - PentaCB	101	80.0
$^{13}C_{12}$ - 2'.3.4.4'.5 - PentaCB	123	80.0
$^{13}C_{12}$ - 2.3'.4.4'.5 - PentaCB	118	82.0
$^{13}C_{12}$ - 2.3.4.4'.5 - PentaCB	114	80.0
$^{13}C_{12}$ - 2.3.3'.4.4' - PentaCB	105	86.8
$^{13}C_{12}$ - 3.3'.4.4'.5 - PentaCB	126	19.9
$^{13}C_{12}$ - 2.2'.4.4'.5.5' - HexaCB	153	80.0
$^{13}C_{12}$ - 2.2'.3.4.4'.5'-HexaCB	138	78.0
$^{13}C_{12}$ - 2.3'.4.4'.5.5'-HexaCB	167	87.6
$^{13}C_{12}$ - 2.3.3'.4.4'.5-HexaCB	156	79.2
$^{13}C_{12}$ - 2.3.3'.4.4'.5'-HexaCB	157	80.8
$^{13}C_{12}$ - 3.3'.4.4'.5.5'- HexaCB	169	18.8
$^{13}C_{12}$ - 2.2'.3.4.4'.5.5'- HeptaCB	180	80.4
$^{13}C_{12}$ - 2.3.3'.4.4'.5.5'- HeptaCB	189	80.0
$^{13}C_{12}$ - 2.2'.3.3'.4.4'.5.5'-OktaCB	194	83.2
$^{13}C_{12}$ - 2.2'.3.3'.4.5.5'.6.6'-NonaCB	208	73.6
$^{13}C_{12}$ - DecaCB	209	88.0

Table S 3 Composition of the $^{13}C_{12}$-PCDD/PCDF quantification standard mixture.

$^{13}C_{12}$-PCDD/PCDF quantification standard	concentration [pg/µL]
$^{13}C_{12}$ - 2.3.7.8 – TCDD	20.0
$^{13}C_{12}$ - 1.2.3.7.8 – PeCDD	12.0
$^{13}C_{12}$ - 1.2.3.4.7.8 - HxCDD	20.0
$^{13}C_{12}$ - 1.2.3.6.7.8 - HxCDD	20.0
$^{13}C_{12}$ - 1.2.3.4.6.7.8 - HpCDD	40.0
$^{13}C_{12}$ – OCDD	40.0
$^{13}C_{12}$ - 2.3.7.8 – TCDF	20.0
$^{13}C_{12}$ - 2.3.4.7.8 - PeCDF	20.0
$^{13}C_{12}$ - 1.2.3.4.7.8 - HxCDF	20.0
$^{13}C_{12}$ - 1.2.3.6.7.8 - HxCDF	20.0
$^{13}C_{12}$ - 2.3.4.6.7.8 - HxCDF	20.0
$^{13}C_{12}$ - 1.2.3.4.6.7.8 - HpCDF	40.0
$^{13}C_{12}$ - OCDF	40.0

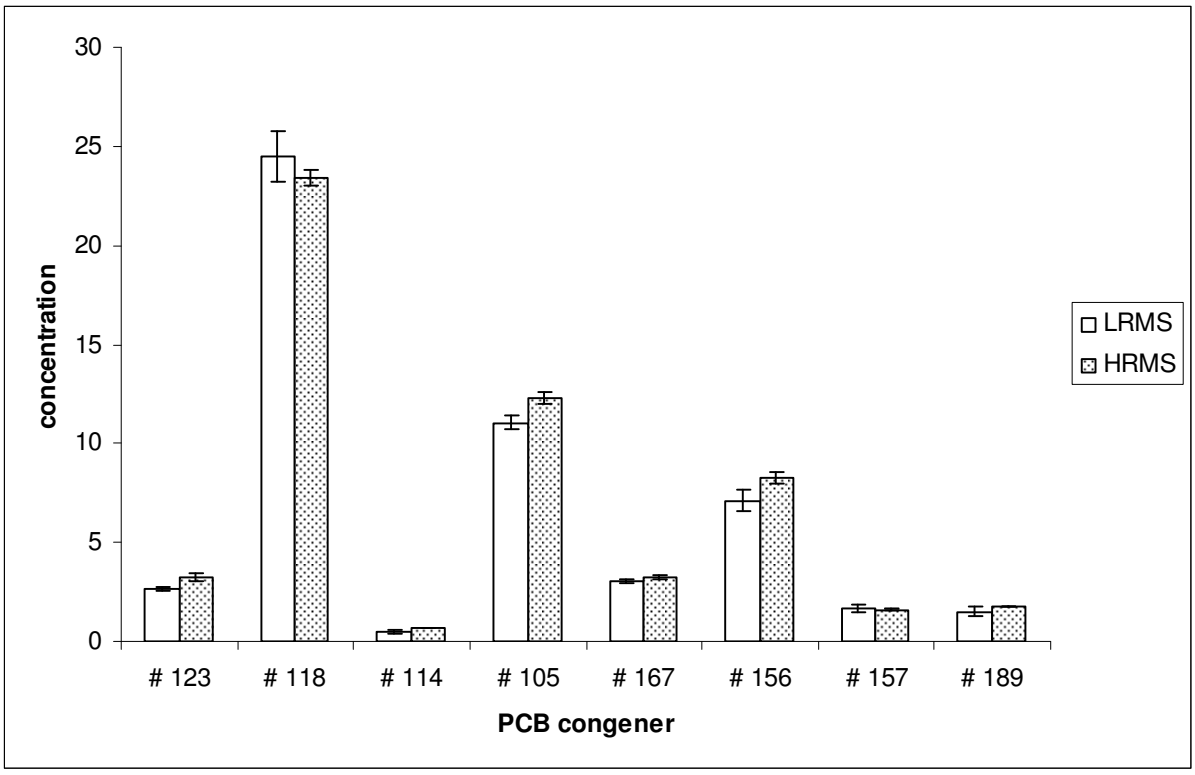


Figure S 1 Comparison of analysed concentrations of dioxin-like PCBs in SRM 1649a with LRMS (white) and HRMS (spotted).

Table S 4 Congener specific and homolog specific determination of PCBs and PCDD/PCDFs in blank samples and NIST SRM 1649a. Deviations are calculated as 95% confidence intervals.

	blank value (PCBs n=7; PCDD/PCDF n=4)	SRM1649a (analysed) (PCBs = LRMS; PCDD/PCDF = HRMS) n=4	SRM1649[ae] (NIST)
PCB homologues	[ng/Sample][a]	[µg/kg][a]	[µg/kg][a]
TriPCBs	2.5 ± 1.2	81 ± 34	---
TetraPCBs	5.8 ± 3.4	148 ± 52	---
PentaPCBs	10 ± 5.9	249 ± 22	---
HexaPCBs	14 ± 8.3	395 ± 50	---
HeptaPCBs	4.6 ± 2.7	256 ± 37	---
OctaPCBs	0.95 ± 0.20b	105 ± 37	---
NonaPCBs	0.043c	16 ± 5.4	---
DecaPCB	0.029 ± 0.0083	5.5 ± 0.98	---
PCB congeners	[ng/Sample][a]	[µg/kg][a]	[µg/kg][a]
PCB #28	0.37 ± 0.17	14 ± 7.3	18.5 ± 1.2
PCB #52	0.66 ± 0.44	18 ± 4.1	24.65 ± 0.97
PCB #101	2.4 ± 1.2	56 ± 8.5	52.9 ± 1.0
PCB #153	2.6 ± 1.4	74 ± 6.5	69.7 ± 7.5
PCB #138	2.9 ± 1.7	73 ± 11	82.5 ± 8.0
PCB #180	1.4 ± 0.65	77 ± 4.8	78.7 ± 8.2
PCB #81	0.013 ± 0.0093	0.45 ± 0.18	---
PCB #77	0.048 ± 0.028	2.1 ± 0.47	---
PCB #126	0.0039 ± 0.0024	0.49 ± 0.20	---
PCB #169	0.0012 ± 0.0047	0.14 ± 0.092	---
PCB #123	0.12 ± 0.092	2.5 ± 0.56	---
PCB #118	0.86 ± 0.48	25 ± 2.5	25.7 ± 1.5
PCB #114	< 0.018 ± 0.0040	0.65 ± 0.18	---
PCB #105	0.22 ± 0.12	12 ± 1.3	8.63 ± 0.80
PCB #167	0.13 ± 0.082	3.0 ± 0.44	---
PCB #156	0.26 ± 0.15	7.6 ± 0.93	16.25 ± 0.77
PCB #157	0.053 ± 0.012	2.0 ± 0.43	---
PCB #189	0.031 ± 0.012	1.9 ± 0.17	---
Total PCB[a]	51 ± 30		---
TEQ excl. LOD[a]	0.00071 ± 0.00039	0.055 ± 0.022	---
TEQ ½ LOD[a]	0.00074 ± 0.00043	0.055 ± 0.022	---
TEQ incl. LOD[a]	0.00076 ± 0.00047	0.055 ± 0.022	---

2. Determination of polychlorinated biphenyls and polychlorinated dibenzo-p-dioxins and dibenzofurans by pressurized liquid extraction and gas chromatography coupled to mass spectrometry in street dust samples

PCDD/PCDF homologues [a]	[pg/Sample]	[µg/kg]	[µg/kg]
TCDD	1.2 ± 0.73[d]	0.23 ± 0.055	0.16 ± 0.080
PCDD	1.5 ± 5.5[d]	1.3 ± 0.17	0.88 ± 0.16
HxCDD	4.6 ± 9.9[d]	6.9 ± 0.45	0.30 ± 0.50
HpCDD	7.4 ± 18	37 ± 4.4	36.4 ± 3.4
OCDD	22 ± 53	214 ± 22	201 ± 20
TCDF	12 ± 44[d]	1.0 ± 0.34	0.52 ± 0.13
PCDF	5.4 ± 31[d]	2.8 ± 0.87	1.6 ± 0.20
HxCDF	4.6 ± 5.2[d]	5.8 ± 1.0	5.0 ± 0.60
HpCDF	3.2 ± 2.3	9.6 ± 2.0	9.8 ± 0.80
OCDF	17 ± 3.4	8.2 ± 1.5	6.8 ± 0.80
PCDD/PCDF congeners	[pg/Sample][a]	[µg/kg]	[µg/kg]
2,3,7,8-TCDD	< 0.11 ± 0.045	0.017 ± 0.0097	0.011 ± 0.0040
1,2,3,7,8-PeCDD	< 0.083 ± 0.052	0.094 ± 0.017	0.091 ± 0.012
1,2,3,4,7,8-HxCDD	< 0.11 ± 0.075	0.22 ± 0.056	0.26 ± 0.020
1,2,3,6,7,8-HxCDD	< 0.088 ± 0.017	0.61 ± 0.13	0.68 ± 0.050
1,2,3,7,8,9-HxCDD	< 0.082 ± 0.042	0.46 ± 0.099	0.64 ± 0.11
1,2,3,4,6,7,8-HpCDD	4.0 ± 9.5	20 ± 2.6	18.8 ± 1.5
2,3,7,8-TCDF	< 0.30 ± 0.44	0.071 ± 0.014	0.068 ± 0.15
1,2,3,7,8-PeCDF	< 0.20 ± 0.24	0.12 ± 0.046	0.090 ± 0.010
2,3,4,7,8-PeCDF	< 0.31 ± 0.71	0.35 ± 0.043	0.28 ± 0.030
1,2,3,4,7,8-HxCDF	< 0.27 ± 0.067	0.57 ± 0.021	0.87 ± 0.26
1,2,3,6,7,8-HxCDF	< 0.12 ± 0.15	0.42 ± 0.034	0.43 ± 0.060
1,2,3,7,8,9-HxCDF	< 0.11 ± 0.018	0.12 ± 0.067	0.066 ± 0.030
2,3,4,6,7,8-HxCDF	< 0.99 ± 1.7	0.67 ± 0.10	0.69 ± 0.030
1,2,3,4,6,7,8-HpCDF	1.8 ± 1.2	4.1 ± 0.33	3.8 ± 0.20
1,2,3,4,7,8,9-HpCDF	< 0.19 ± 0.12	0.41 ± 0.11	0.46 ± 0.070
TEQ excl. LOD	0.30 ± 0.13	0.85 ± 0.094	0.86 ± 0.060
TEQ ½ LOD	0.57 ± 0.22	0.85 ± 0.094	0.86 ± 0.060
TEQ incl. LOD	0.84 ± 0.30	0.85 ± 0.094	0.86 ± 0.060

a = Uncertainties are expressed as an expanded uncertainty at the 95 % level of confidence. For the calculation of the confidence interval for PCB analysis seven single analyses were taken into account. The calculation of the confidence level for PCDD/PCDF was based on four individual analyses, respectively.

b = Aberrant from superscription a only four analysis were used for the calculation of the confidence interval.

c = No confidence interval could be calculated. Homologue group could only be detected in one determination.

d = Aberrant from superscription a only duplicate analysis were used for the calculation of the confidence interval.

e = Certified concentrations and confidence intervals for PCBs and reference concentrations and confidence intervals for PCDD/PCDFs were taken from the certificate of analysis provided by NIST [NIST, 2007].

Recoveries of individual PCDD/PCDFs in a real street dust sample and SRM 1649a for Soxhlet extraction and PLE

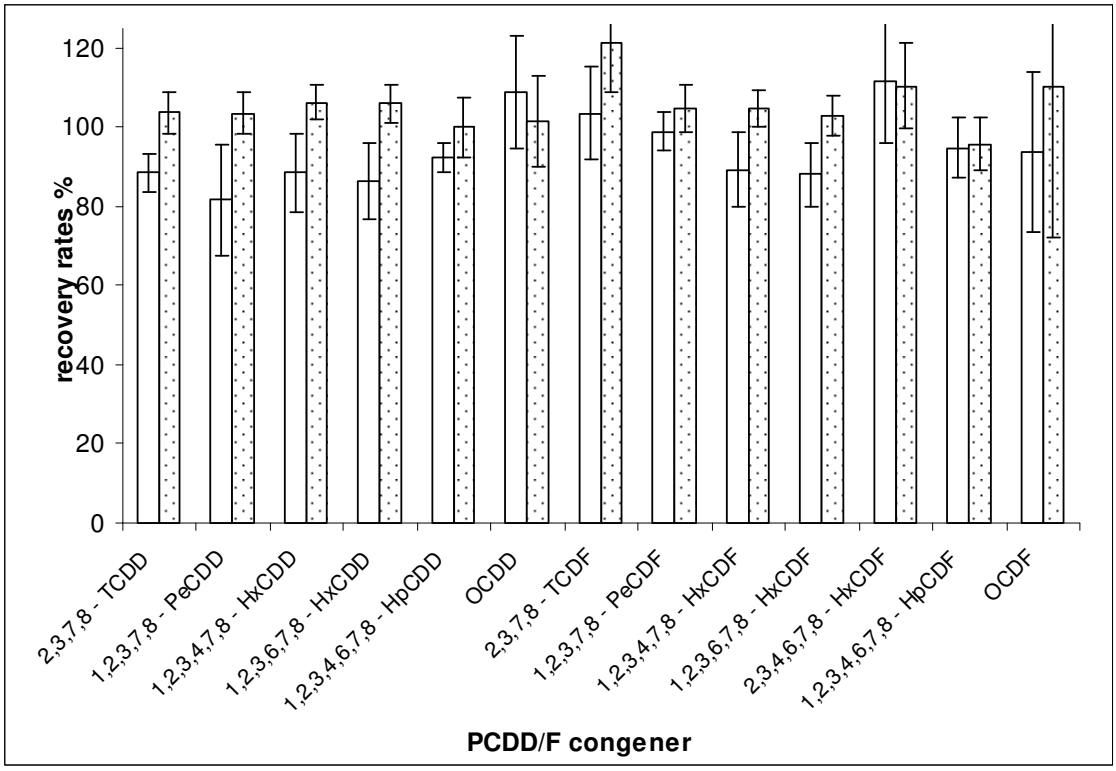


Figure S 2 Recoveries of individual PCDD/PCDF congener for Soxhlet (blank) and PLE (spotted) of a real dust sample. In addition standard deviation for n=3 are given.

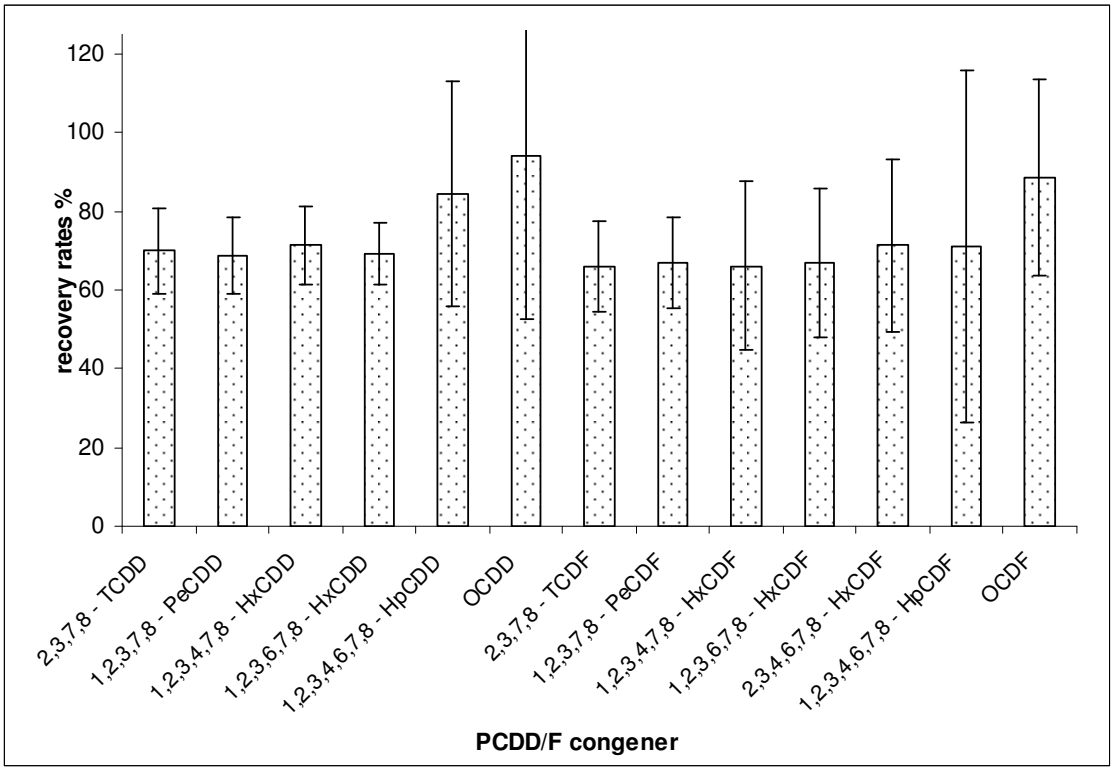


Figure S 3 Recoveries of individual PCDD/PCDF congener for PLE of NIST SRM 1649a. In addition standard deviation for n=4 are given.

Table S 5 Recoveries of individual PCDD/PCDF congener for PLE and Soxhlet of a real dust sample and recoveries of individual PCDD/PCDF congeners after PLE of NIST SRM 1649a. In addition standard deviations are given.

PCDD/PCDF congener	Absolute recovery rate [%]		
	real dust sample		SRM 1649a
	Soxhlet (n=3)	PLE (n=3)	PLE (n=4)
2,3,7,8 - TCDD	88 ± 5.0	104 ± 5.2	70 ± 11
1,2,3,7,8 - PeCDD	82 ± 14	104 ± 5.4	69 ± 9.8
1,2,3,4,7,8 - HxCDD	89 ± 10	106 ± 4.2	71 ± 9.8
1,2,3,6,7,8 - HxCDD	86 ± 9.6	106 ± 4.8	69 ± 7.8
1,2,3,4,6,7,8 - HpCDD	92 ± 3.7	100 ± 7.6	84 ± 28
OCDD	109 ± 14	102 ± 12	94 ± 42
2,3,7,8 - TCDF	104 ± 12	121 ± 12	66 ± 12
1,2,3,7,8 - PeCDF	99 ± 4.9	105 ± 6.0	67 ± 11
1,2,3,4,7,8 - HxCDF	89 ± 9.3	105 ± 4.6	66 ± 21
1,2,3,6,7,8 - HxCDF	88 ± 8.0	103 ± 5.1	67 ± 19
2,3,4,6,7,8 - HxCDF	112 ± 16	110 ± 11	71 ± 22
1,2,3,4,6,7,8 - HpCDF	95 ± 7.7	96 ± 6.6	71 ± 45
OCDF	94 ± 20	108 ± 41	103 ± 42

Table S 6 Overview of recorded qualification and quantification (bold) m/z and their relative isotope ratios for PCB analysis (LRMS).

PCB						
No. of Cl atoms	m/z (^{12}C)		m/z (^{13}C)		relative isotope ratio %	
3	256	258	268	270	100	97
4	290	292	302	304	78	100
5	326	328	338	340	100	64
6	360	362	372	374	100	80
7	394	396	406	408	100	96
8	428	430	440	442	89	100
9	462	464	474	476	78	100
10	498	500	510	512	100	86

Table S 7 Overview of recorded qualification and quantification (bold) m/z and their relative isotope ratios for PCDD/PCDF analysis (HRMS).

PCDD/PCDF						
No. of Cl atoms (D=PCDD; F=PCDF)	m/z (^{12}C)		m/z (^{13}C)		relative isotope ratio %	
D4	319.8965	321.8936	331.9368	333.9339	78	100
D5	355.8546	357.8517	357.8517	369.8920	100	64
D6	389.8156	391.8127	401.8559	403.8530	100	80
D7	423.7767	425.7737	435.8170	437.8140	100	96
D8	457.7377	459.7348	469.7780	471.7751	89	100
F4	303.9016	305.8987	315.9419	317.9390	78	100
F5	339.8597	341.8568	351.9000	353.8971	100	64
F6	373.8207	375.8178	385.8610	387.8581	100	80
F7	407.7818	409.7788	419.8221	421.8191	100	96
F8	441.7428	443.7398	453.7831	455.7801	89	100

Table S 8 Standard solutions (CS1 - CS5) and concentrations of the individual $^{12}C_{12}$-PCB- and $^{13}C_{12}$-PCB congener in pg/µl and the equation of calibration (y = b • x + a) and the belonging correlation coefficient (r^2) for calibrated $^{12}C_{12}$-PCB congeners

$^{12}C_{12}$-PCB #	CS1	CS2	CS3	CS4	CS5	b	a	r^2
28	10	25	50	150	200	1.2046	- 0.0498	0.9994
52	10	25	50	150	200	1.1645	- 0.0402	0.9988
101	10	25	50	150	200	0.9822	- 0.0269	0.9986
123	4.0	10	20	60	80	1.0572	- 0.0173	0.9987
118	4.0	10	20	60	80	1.0429	- 0.0239	0.9975
114	4.0	10	20	60	80	1.1293	- 0.0196	0.9975
105	4.0	10	20	60	80	0.9907	- 0.0171	0.9981
153	10	25	50	150	200	1.1474	- 0.0314	0.9975
138	10	25	50	150	200	1.1008	- 0.0324	0.9983
167	4.0	10	20	60	80	0.9758	- 0.0125	0.9981
156	4.0	10	20	60	80	0.9891	- 0.0145	0.9982
157	4.0	10	20	60	80	1.0334	- 0.0149	0.9968
180	10	25	50	150	200	0.9502	- 0.036	0.9974
189	4.0	10	20	60	80	0.9889	- 0.0082	0.9986
194	20	50	100	300	400	1.0477	- 0.060	0.9982
208	20	50	100	300	400	1.0439	- 0.0579	0.9987
209	10	25	50	150	200	1.0218	- 0.0225	0.9988
$^{13}C_{12}$-PCB #								
28	80.0	80.0	80.0	80.0	80.0	-	-	-
52	78.8	78.8	78.8	78.8	78.8	-	-	-
101	80.0	80.0	80.0	80.0	80.0	-	-	-
123	80.0	80.0	80.0	80.0	80.0	-	-	-
118	82.0	82.0	82.0	82.0	82.0	-	-	-
114	80.0	80.0	80.0	80.0	80.0	-	-	-
105	86.8	86.8	86.8	86.8	86.8	-	-	-
153	80.0	80.0	80.0	80.0	80.0	-	-	-
138	78.0	78.0	78.0	78.0	78.0	-	-	-
128	80.0	80.0	80.0	80.0	80.0	-	-	-
167	87.6	87.6	87.6	87.6	87.6	-	-	-
156	79.2	79.2	79.2	79.2	79.2	-	-	-
157	80.8	80.8	80.8	80.8	80.8	-	-	-
180	80.4	80.4	80.4	80.4	80.4	-	-	-
189	80.0	80.0	80.0	80.0	80.0	-	-	-
194	83.2	83.2	83.2	83.2	83.2	-	-	-
208	73.6	73.6	73.6	73.6	73.6	-	-	-
209	88.0	88.0	88.0	88.0	88.0	-	-	-

Table S 9 Standard solutions (CS1 - CS5) and concentrations of the individual $^{12}C_{12}$-PCDD/PCDF- and $^{13}C_{12}$-PCDD/PCDF congener in pg/µl and the equation of calibration (y = b • x + a) and the belonging correlation coefficient (r^2) for calibrated $^{12}C_{12}$-PCDD/PCDF congeners

$^{12}C_{12}$-PCDD/PCDF	CS1	CS2	CS3	CS4	CS5	b	a	r2
2,3,7,8 - TCDD	0.080	0.24	0.40	10	30	0.8796	- 0.0018	0.9984
1,2,3,7,8 - PeCDD	0.40	1.2	2.0	50	150	1.0409	- 0.0594	0.9980
1,2,3,4,7,8 - HxCDD	0.40	1.2	2.0	50	150	1.2684	- 0.0251	0.9988
1,2,3,6,7,8 - HxCDD	0.40	1.2	2.0	50	150	1.2352	- 0.0304	0.9983
1,2,3,7,8,9 - HxCDD	0.40	1.2	2.0	50	150	1.2909	- 0.0411	0.9957
1,2,3,4,6,7,8 - HpCDD	0.40	1.2	2.0	50	150	1.0884	- 0.0089	0.9995
OCDD	0.80	2.4	4.0	100	300	0.8782	- 0.0101	0.9996
2,3,7,8 - TCDF	0.080	0.24	0.40	10	30	1.0719	- 0.0037	0.9989
1,2,3,7,8 - PeCDF	0.40	1.2	2.0	50	150	0.8446	+ 0.0168	0.9990
2,3,4,7,8 - PeCDF	0.40	1.2	2.0	50	150	1.123	- 0.025	0.9995
1,2,3,4,7,8 - HxCDF	0.40	1.2	2.0	50	150	1.1563	- 0.0438	0.9983
1,2,3,6,7,8 - HxCDF	0.40	1.2	2.0	50	150	1.102	- 0.0333	0.9990
1,2,3,7,8,9 - HxCDF	0.40	1.2	2.0	50	150	0.876	- 0.019	0.9980
2,3,4,6,7,8 - HxCDF	0.40	1.2	2.0	50	150	0.985	- 0.0224	0.9991
1,2,3,4,6,7,8 - HpCDF	0.40	1.2	2.0	50	150	1.1052	- 0.0088	0.9993
1,2,3,4,7,8,9 - HpCDF	0.40	1.2	2.0	50	150	0.7592	- 0.0201	0.9970
OCDF	0.80	2.4	4.0	100	300	1.0454	- 0.0233	0.9987
$^{13}C_{12}$-PCDD/PCDF								
2,3,7,8 - TCDD	20	20	20	20	20	-	-	-
1,2,3,4 - TCDD	20	20	20	20	20	-	-	-
1,2,3,7,8 - PeCDD	12	12	12	12	12	-	-	-
1,2,3,4,7,8 - HxCDD	20	20	20	20	20	-	-	-
1,2,3,6,7,8 - HxCDD	20	20	20	20	20	-	-	-
1,2,3,7,8,9 - HxCDD	20	20	20	20	20	-	-	-
1,2,3,4,6,7,8 - HpCDD	40	40	40	40	40	-	-	-
OCDD	40	40	40	40	40	-	-	-
2,3,7,8 - TCDF	20	20	20	20	20	-	-	-
2,3,4,7,8 - PeCDF	20	20	20	20	20	-	-	-
1,2,3,4,7,8 - HxCDF	20	20	20	20	20	-	-	-
1,2,3,6,7,8 - HxCDF	20	20	20	20	20	-	-	-
2,3,4,6,7,8 - HxCDF	20	20	20	20	20	-	-	-
1,2,3,4,6,7,8 - HpCDF	40	40	40	40	40	-	-	-
OCDF	40	40	40	40	40	-	-	-

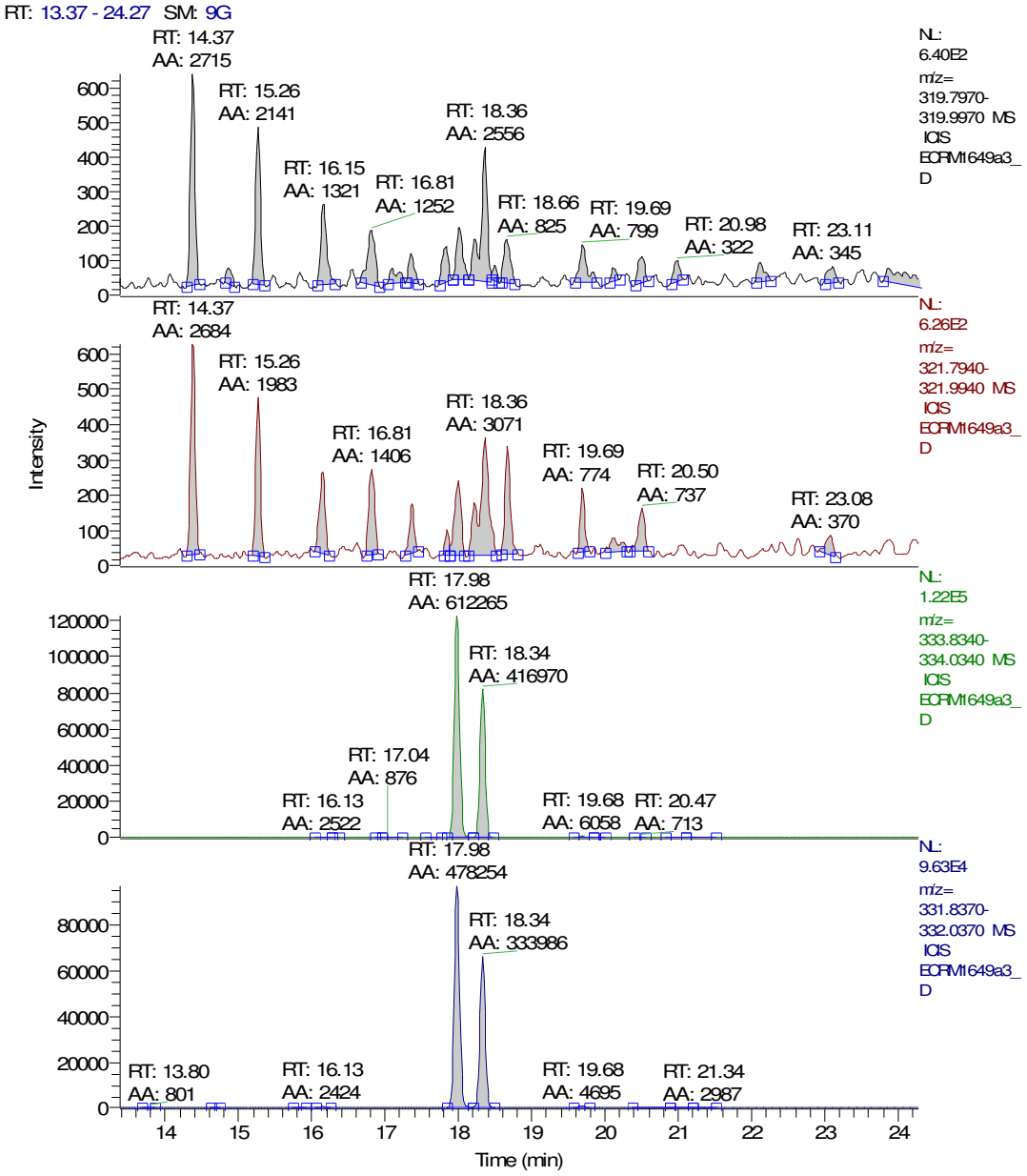


Figure S 4 Chromatogram in selected ion monitoring mode for TCDD of NIST SRM 1649a

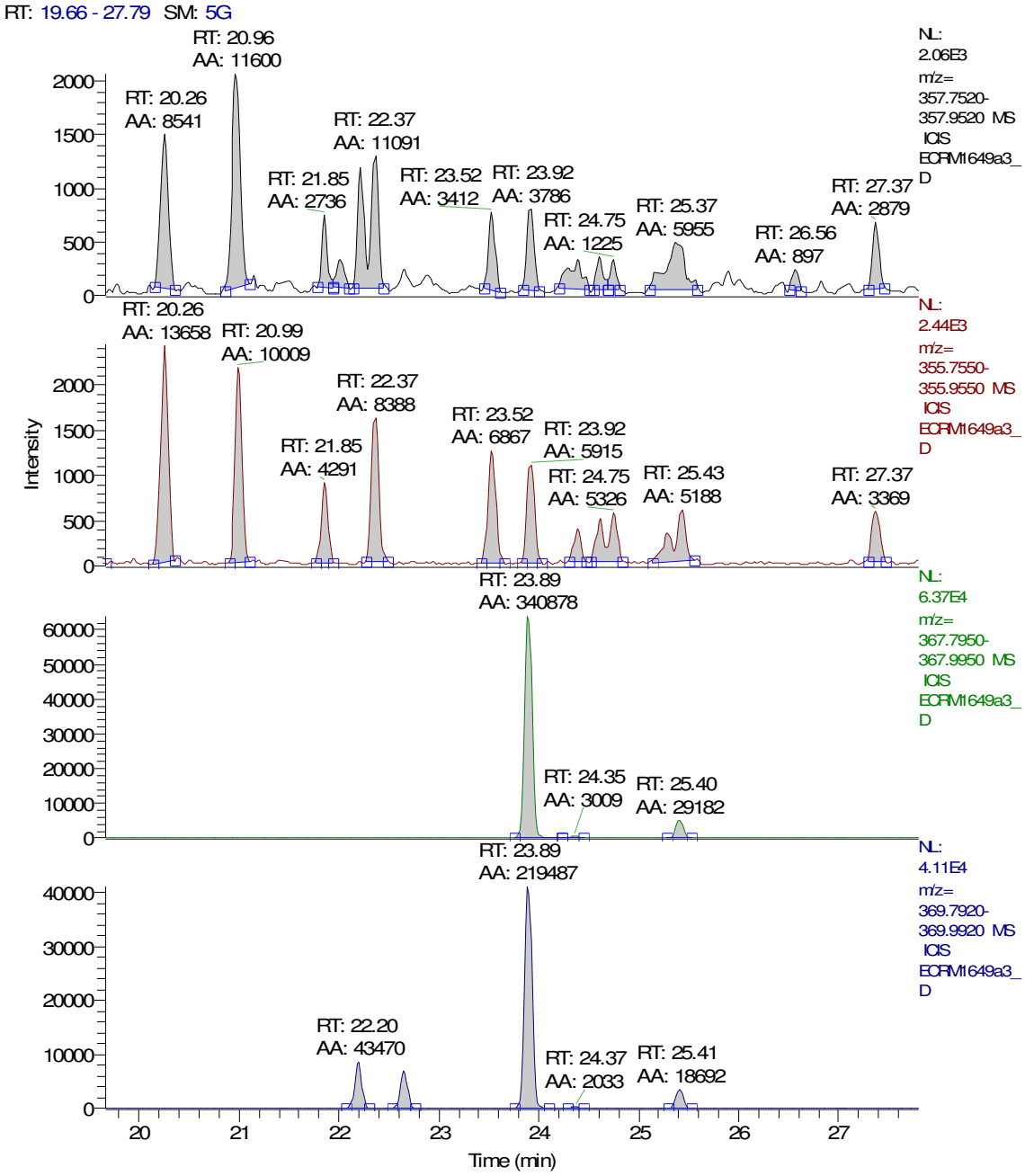


Figure S 5 Chromatogram in selected ion monitoring mode for PeCDD of NIST SRM 1649a

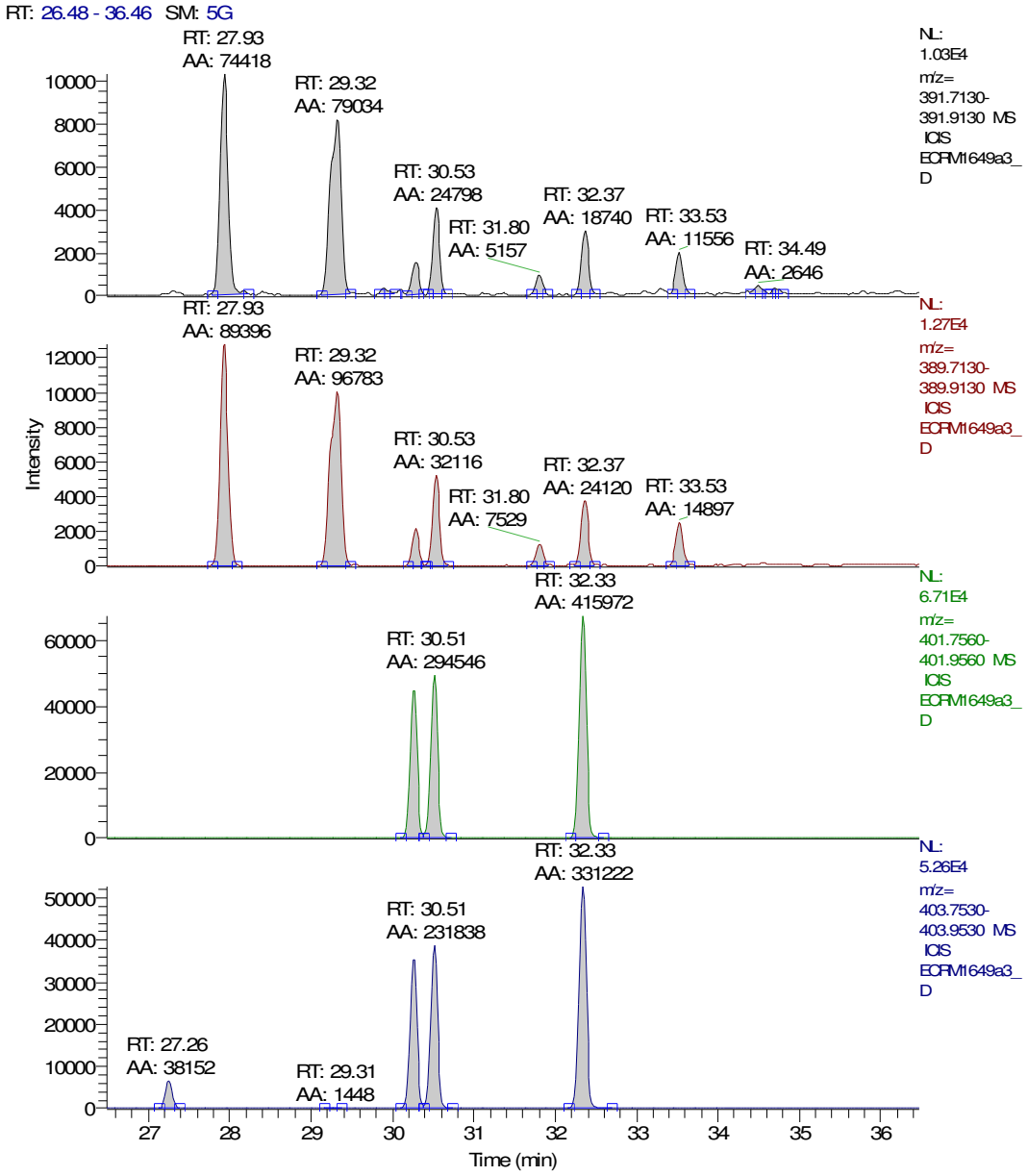


Figure S 6 Chromatogram in selected ion monitoring mode for HxCDD of NIST SRM 1649a.

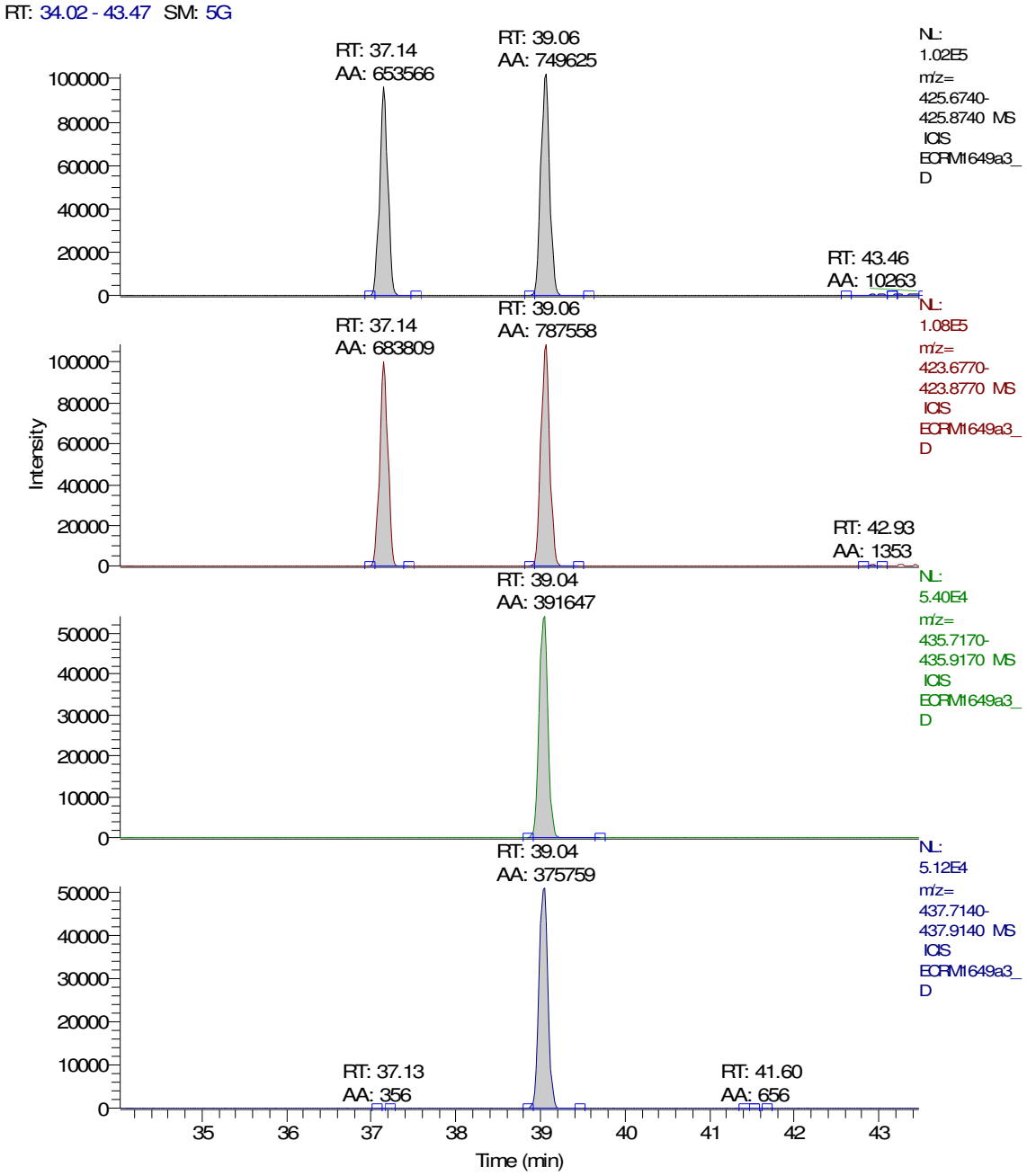


Figure S 7 Chromatogram in selected ion monitoring mode for HpCDD of NIST SRM 1649a.

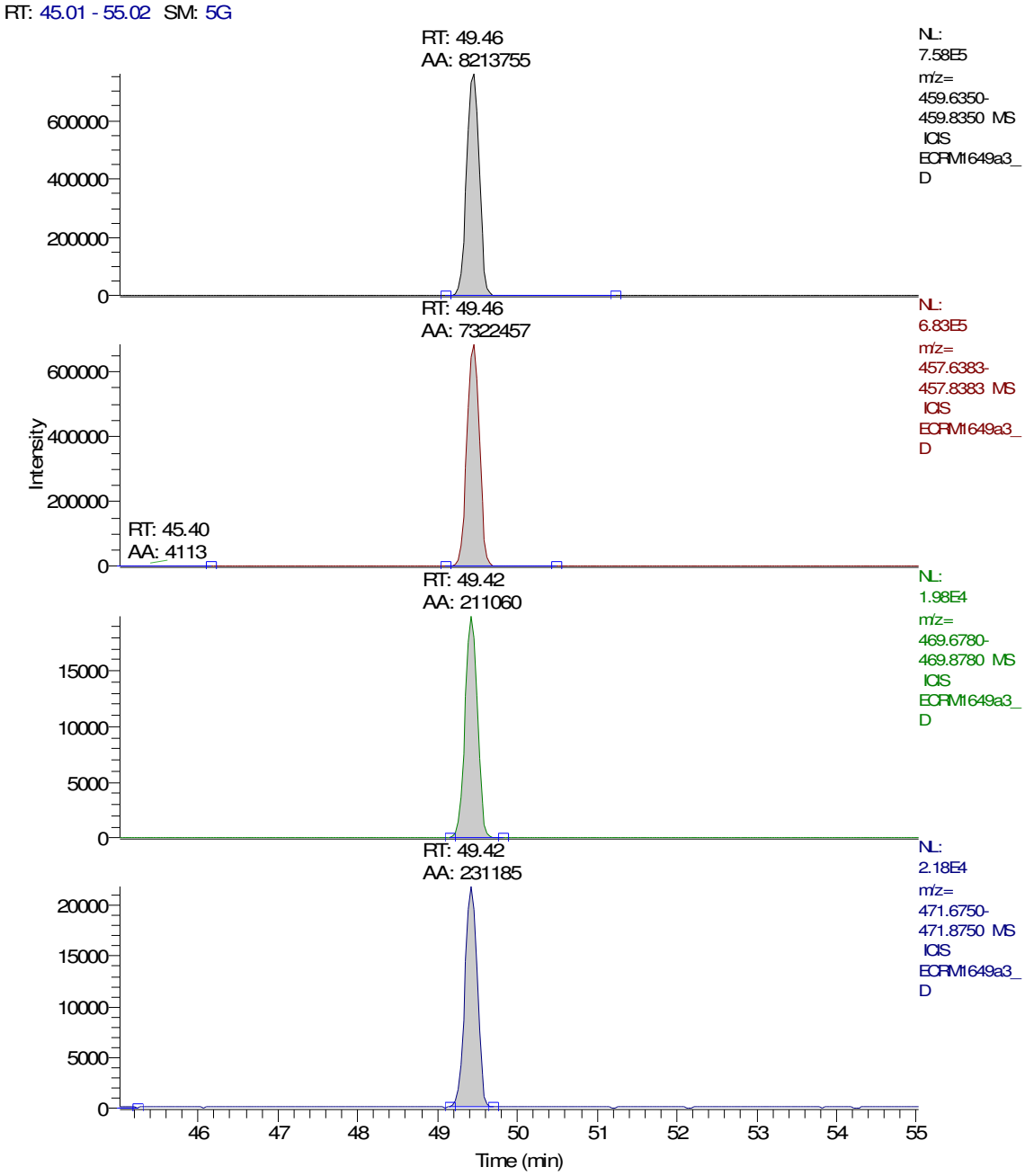


Figure S 8 Chromatogram in selected ion monitoring mode for OCDD of NIST SRM 1649a.

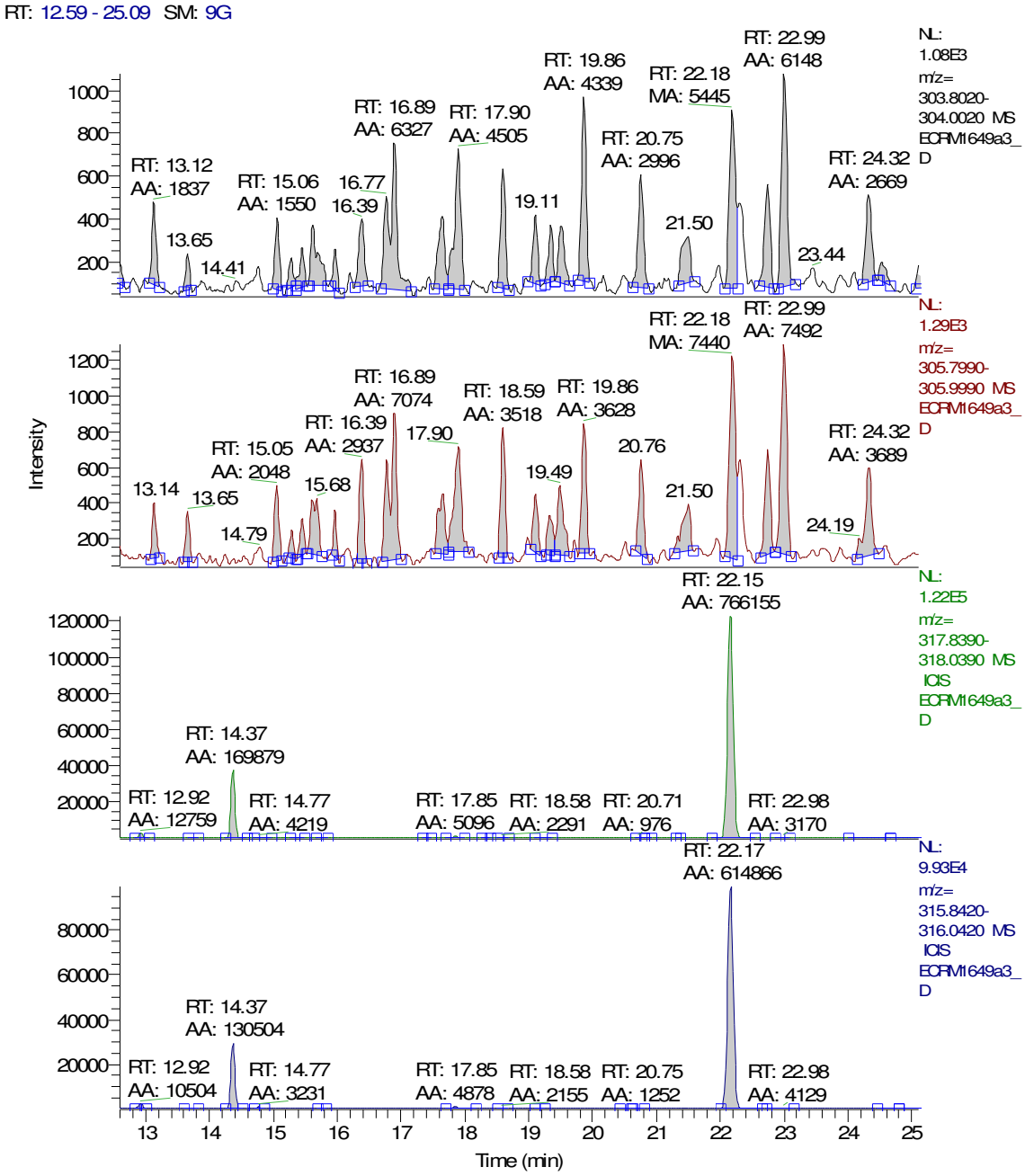


Figure S 9 Chromatogram in selected ion monitoring mode for TCDF of NIST SRM 1649a.

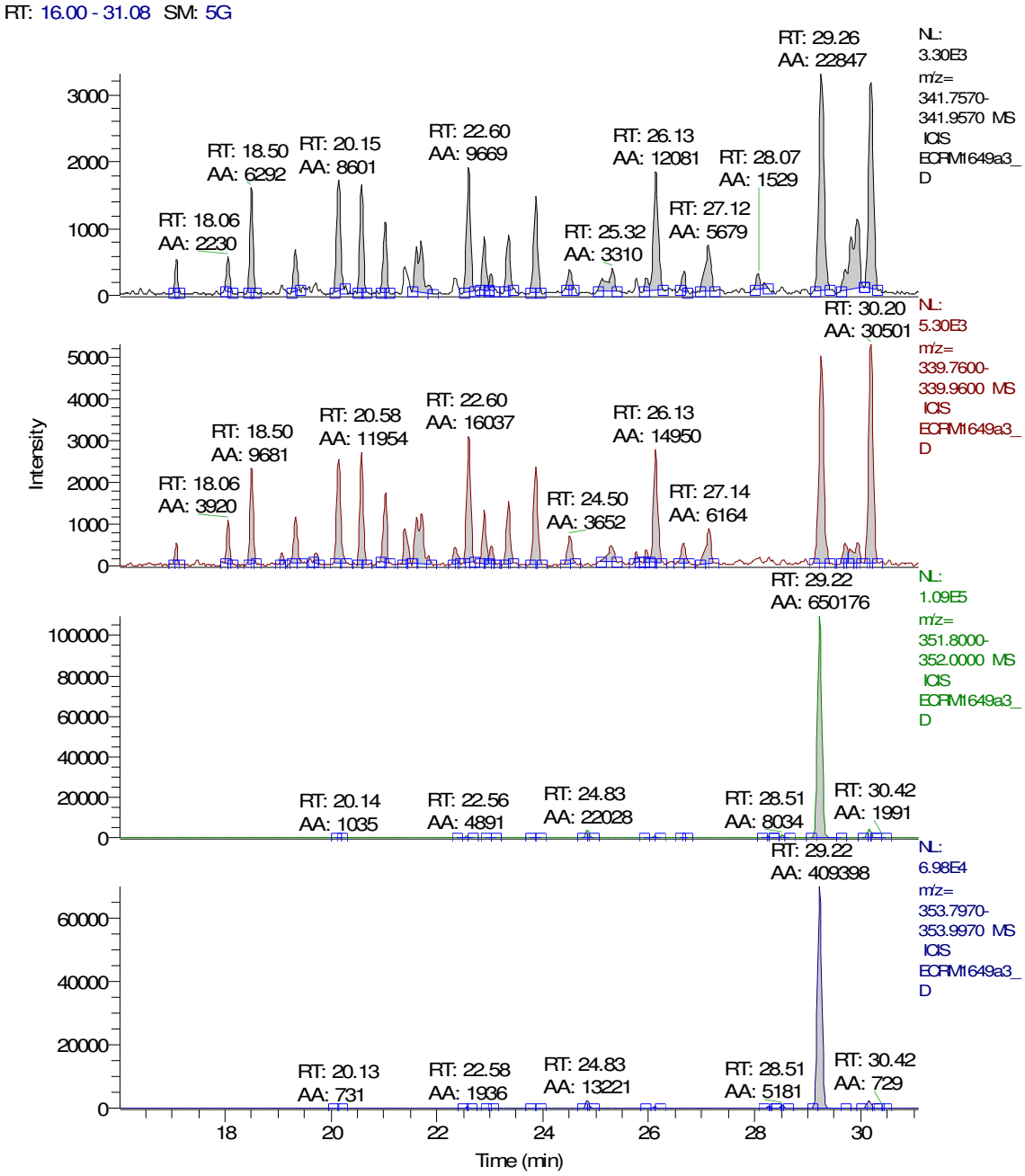


Figure S 10 Chromatogram in selected ion monitoring mode for PeCDF of NIST SRM 1649a.

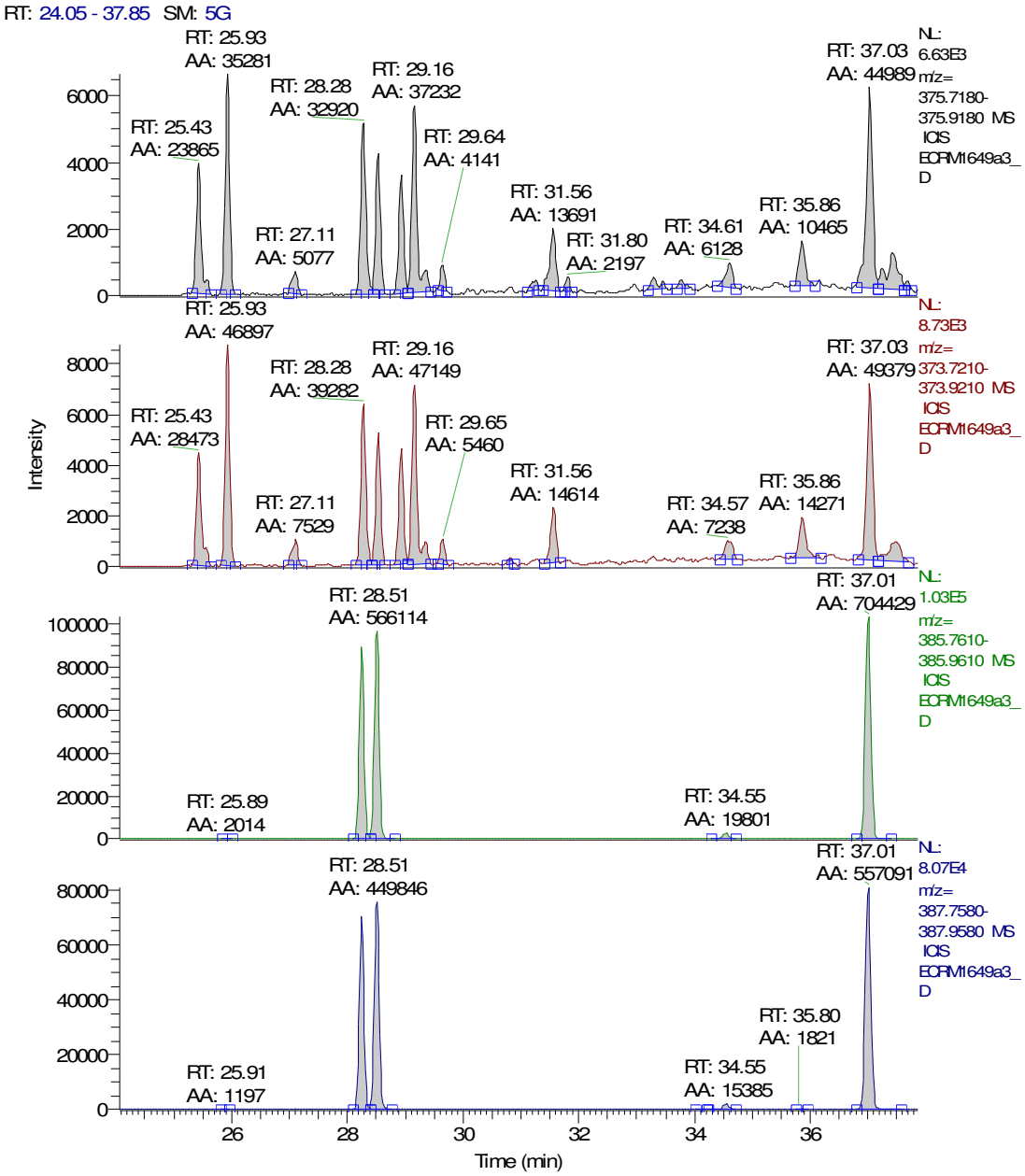


Figure S 11 Chromatogram in selected ion monitoring mode for HxCDF of NIST SRM 1649a.

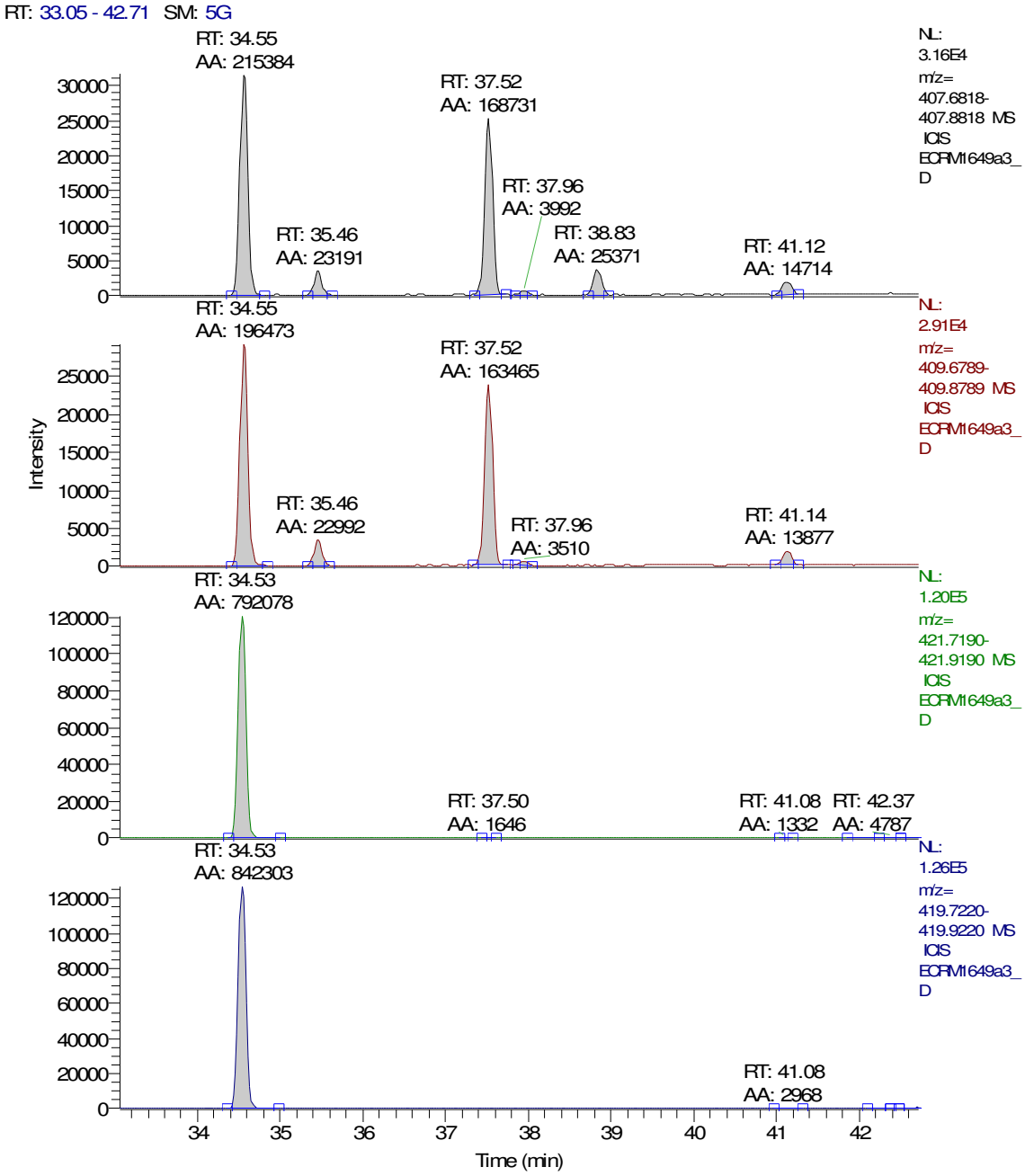


Figure S 12 Chromatogram in selected ion monitoring mode for HpCDF of NIST SRM 1649a.

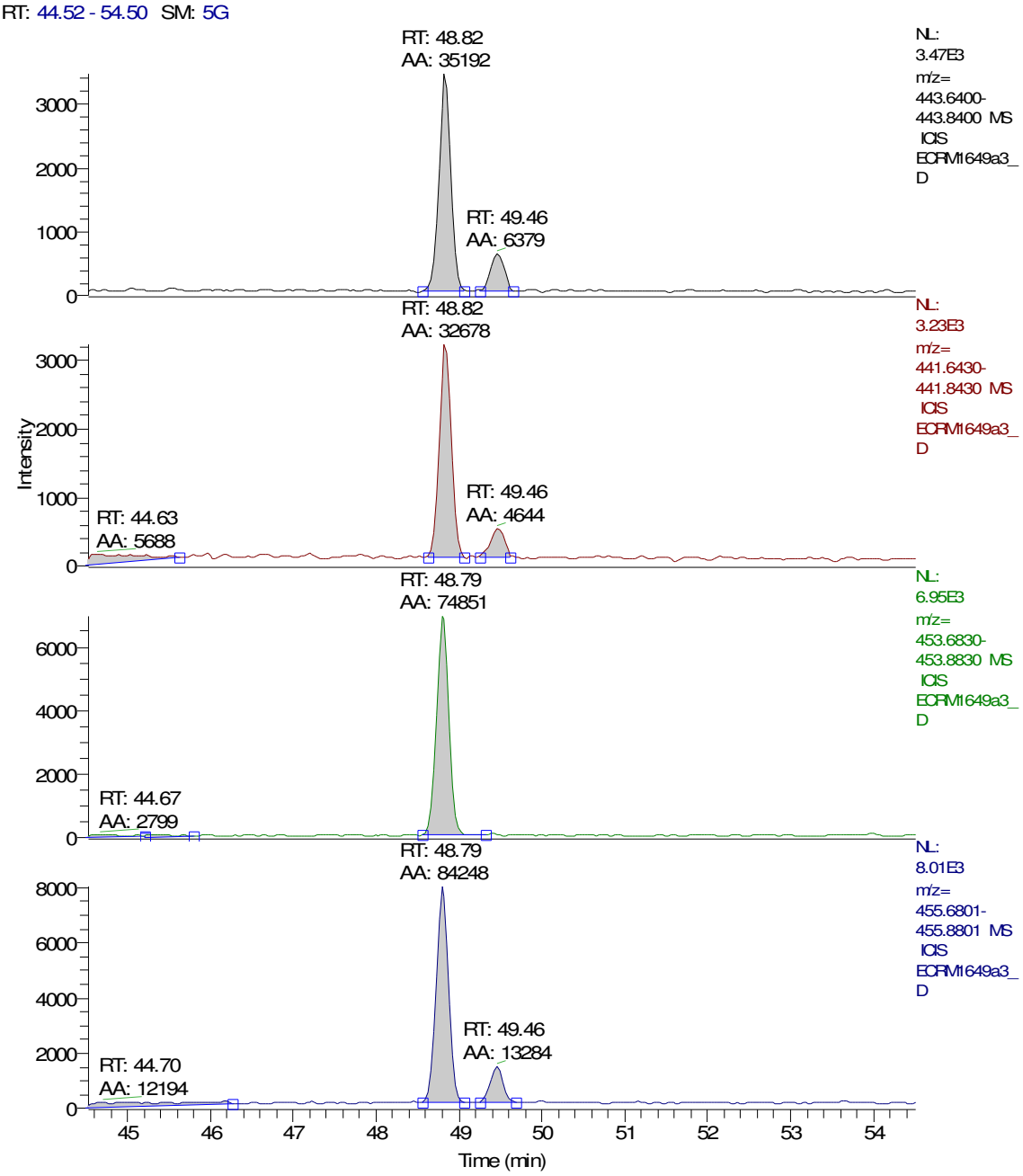


Figure S 13 Chromatogram in selected ion monitoring mode for OCDF of NIST SRM 1649a.

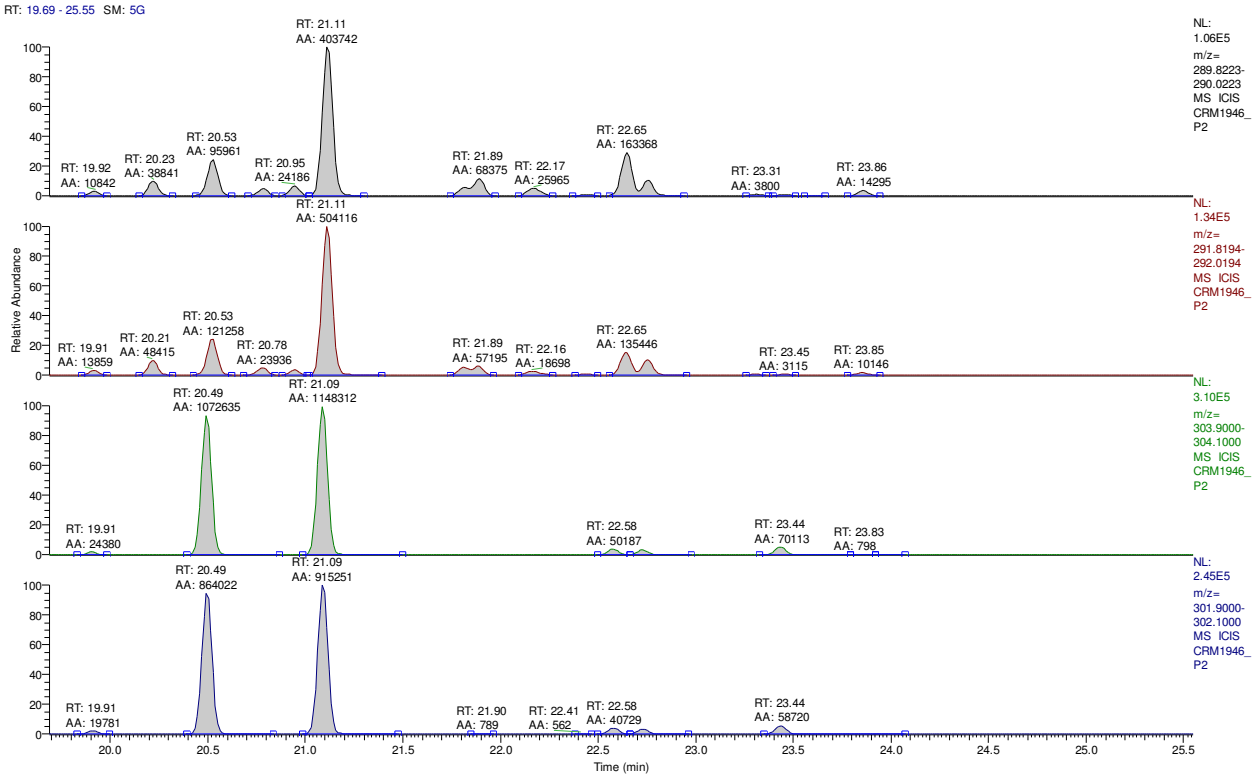


Figure S 14 Chromatogram in selected ion monitoring mode for PCB #77 and PCB #81 of NIST SRM 1649a.

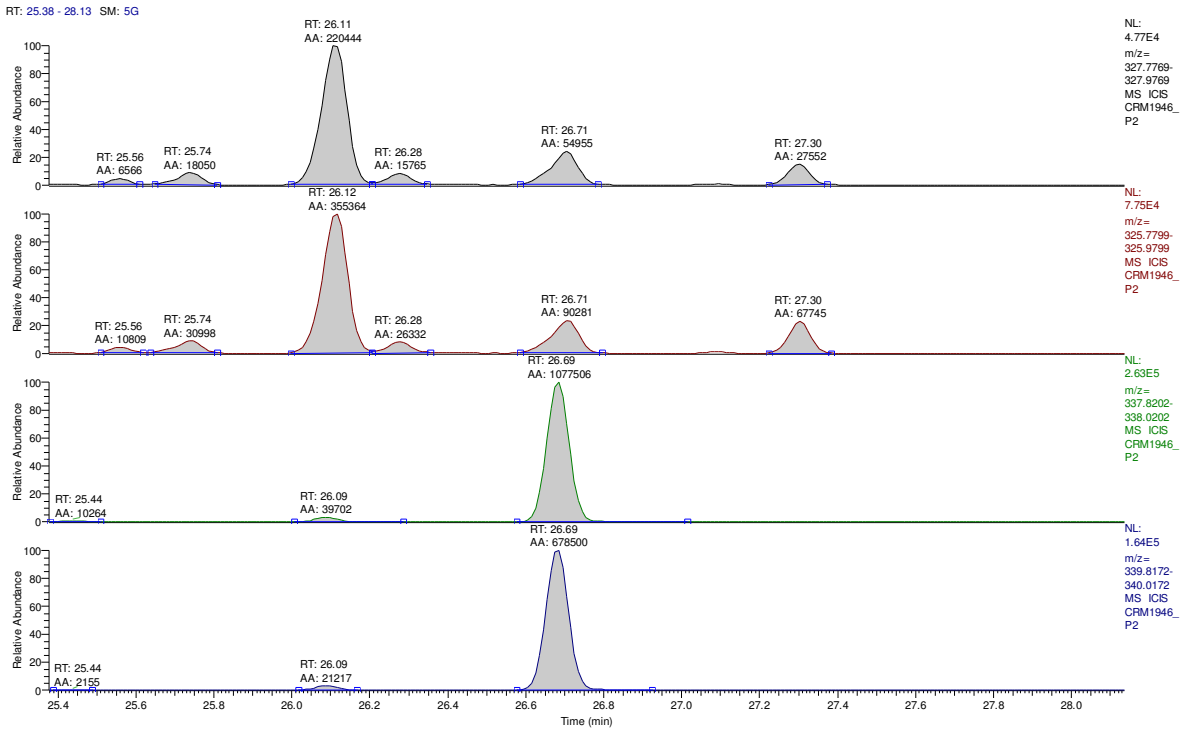


Figure S 15 Chromatogram in selected ion monitoring mode for PCB #126 of NIST SRM 1649a

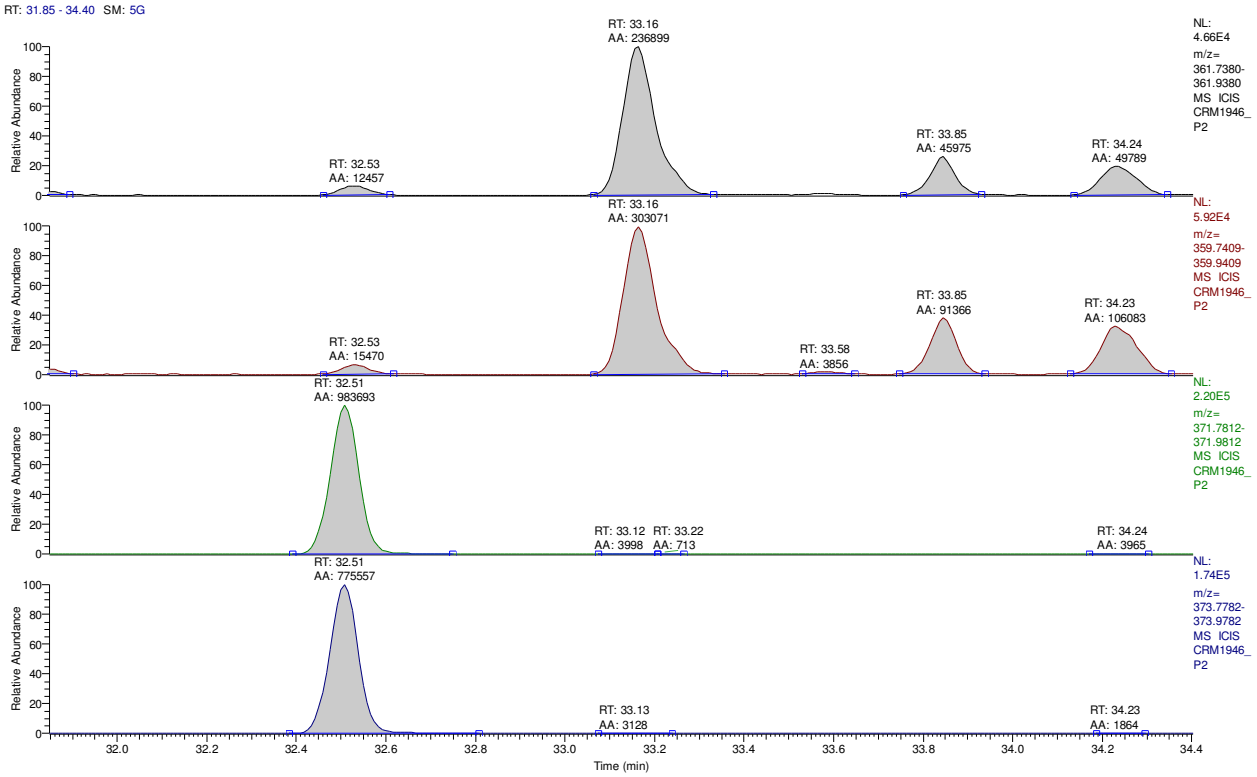


Figure S 16 Chromatogram in selected ion monitoring mode for PCB #169 of NIST SRM 1649a.

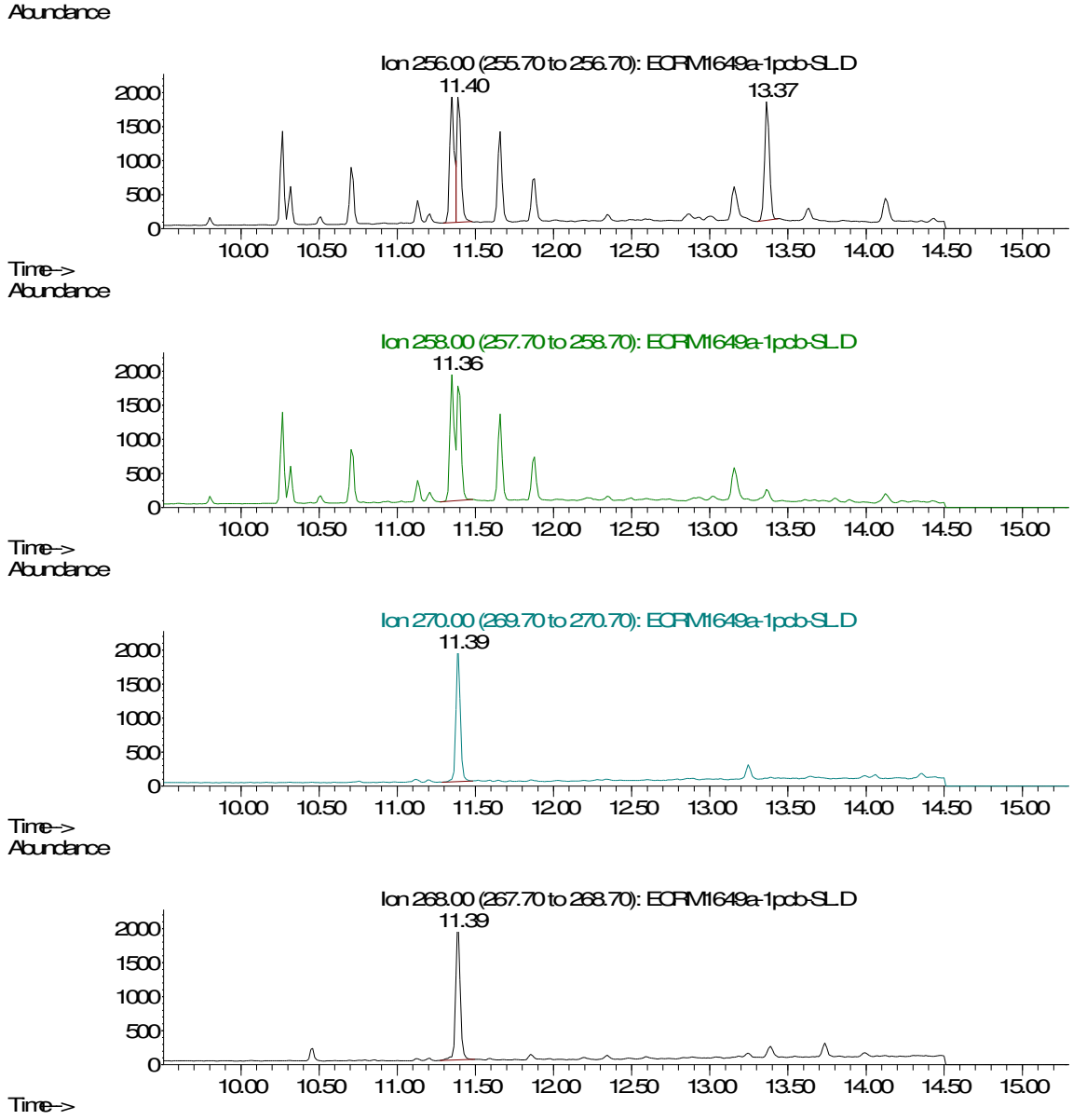


Figure S 17 Chromatogram in selected ion monitoring mode for TriPCBs of NIST SRM 1649a.

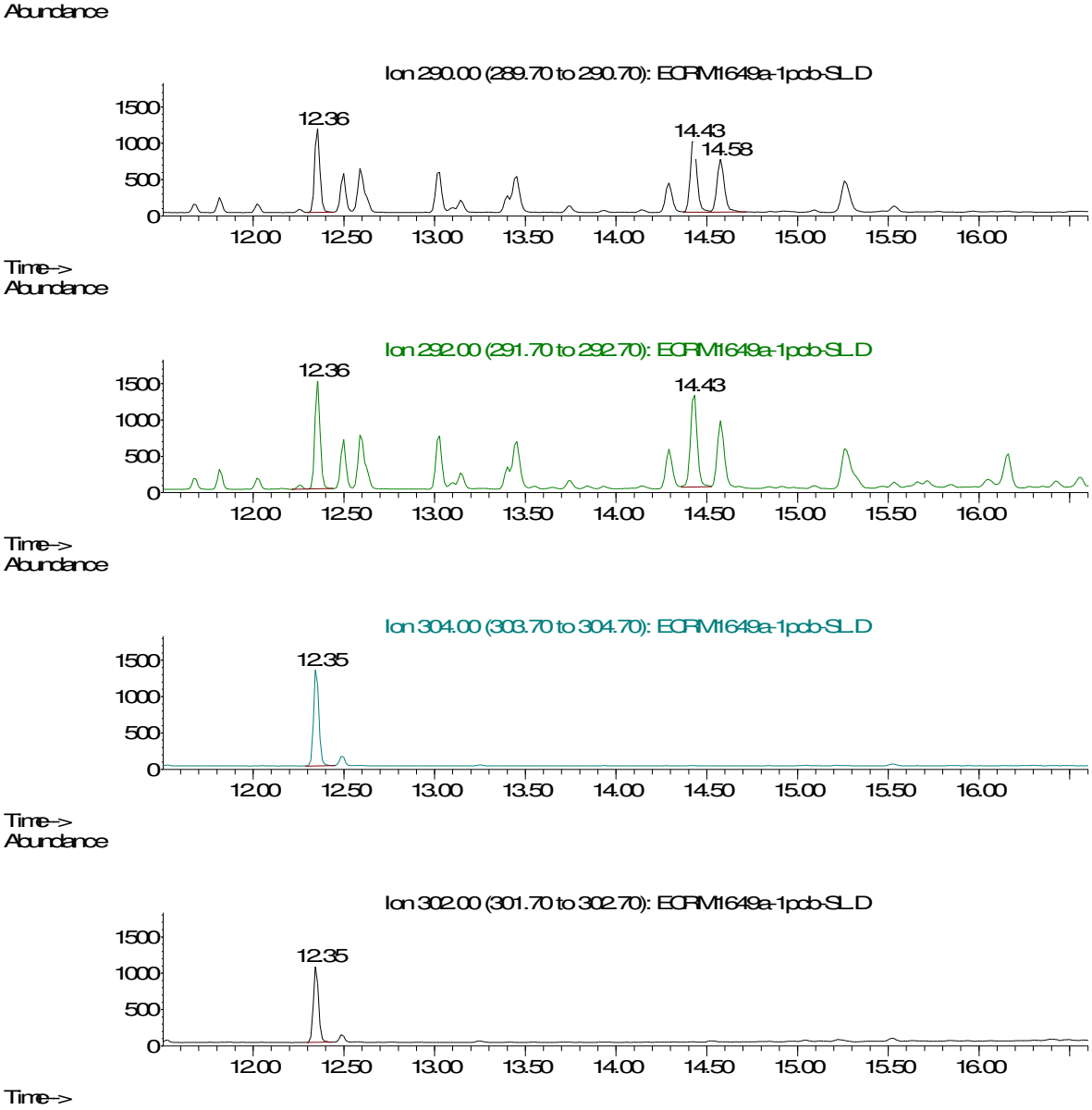


Figure S 18 Chromatogram in selected ion monitoring mode for TetraPCBs of NIST SRM 1649a.

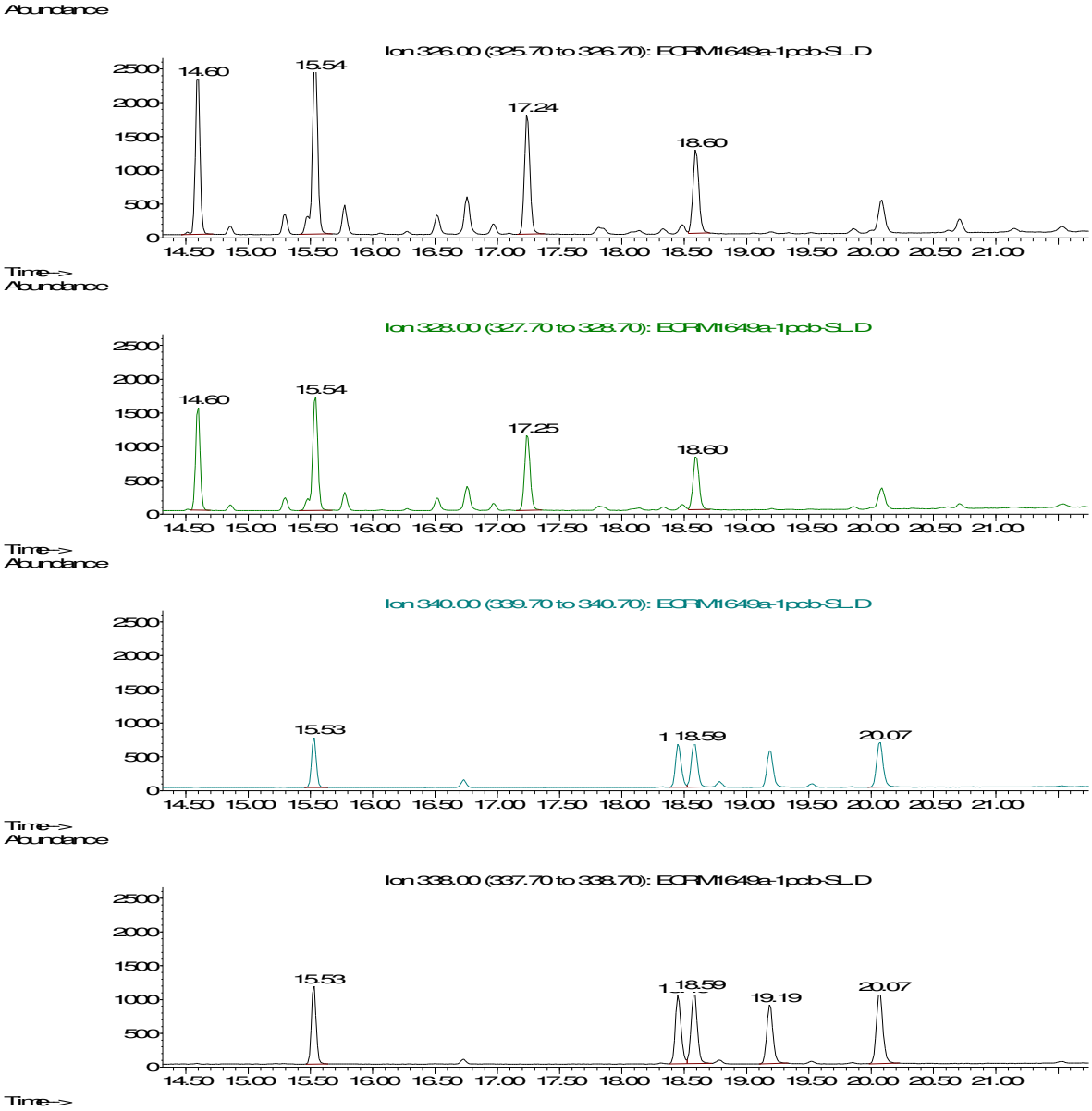


Figure S 19 Chromatogram in selected ion monitoring mode for PentaPCBs of NIST SRM 1649a.

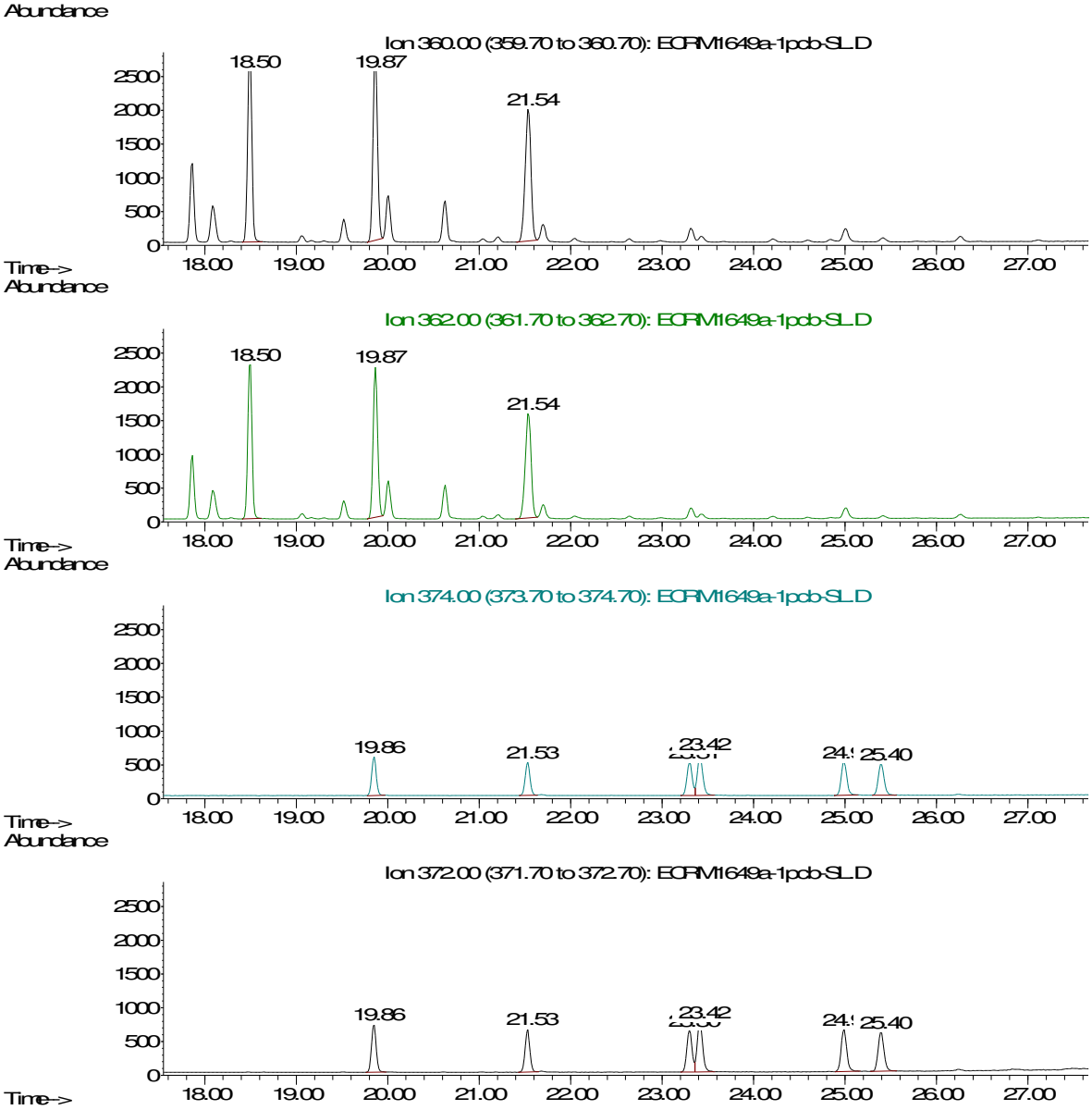


Figure S 20 Chromatogram in selected ion monitoring mode for HexaPCBs of NIST SRM 1649a.

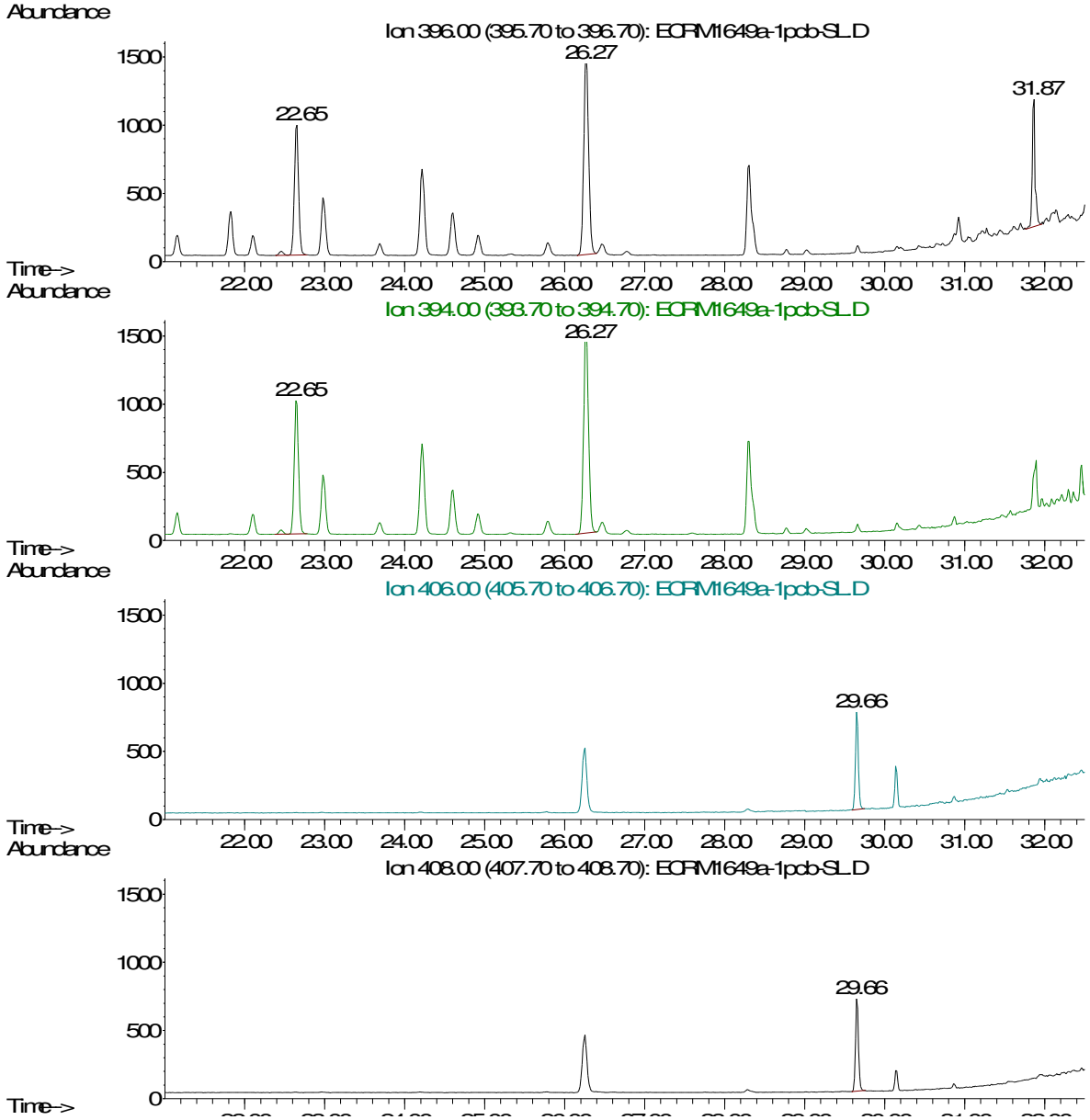


Figure S 21 Chromatogram in selected ion monitoring mode for HeptaPCBs of NIST SRM 1649a.

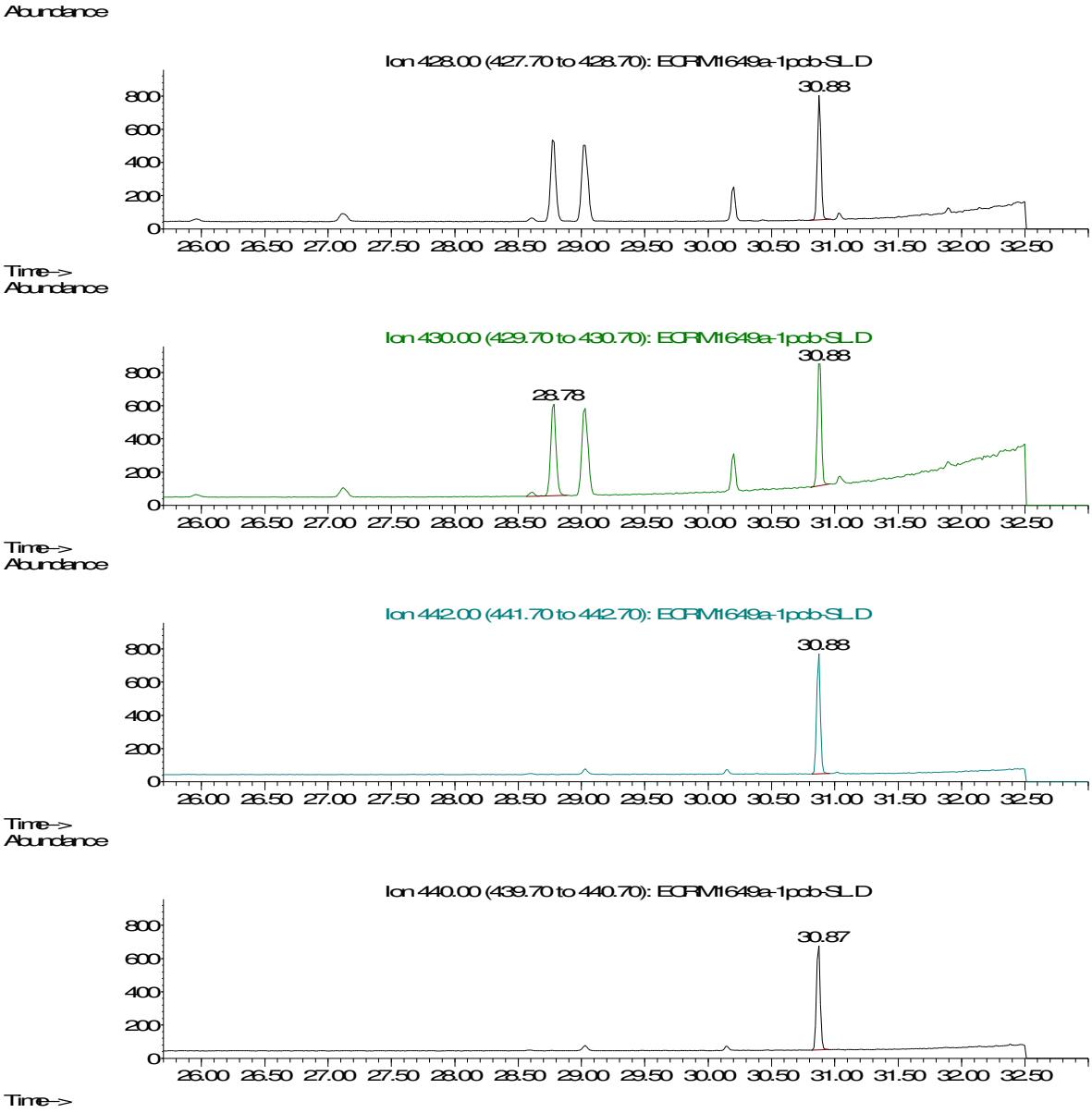


Figure S 22 Chromatogram in selected ion monitoring mode for OctaPCBs of NIST SRM 1649a.

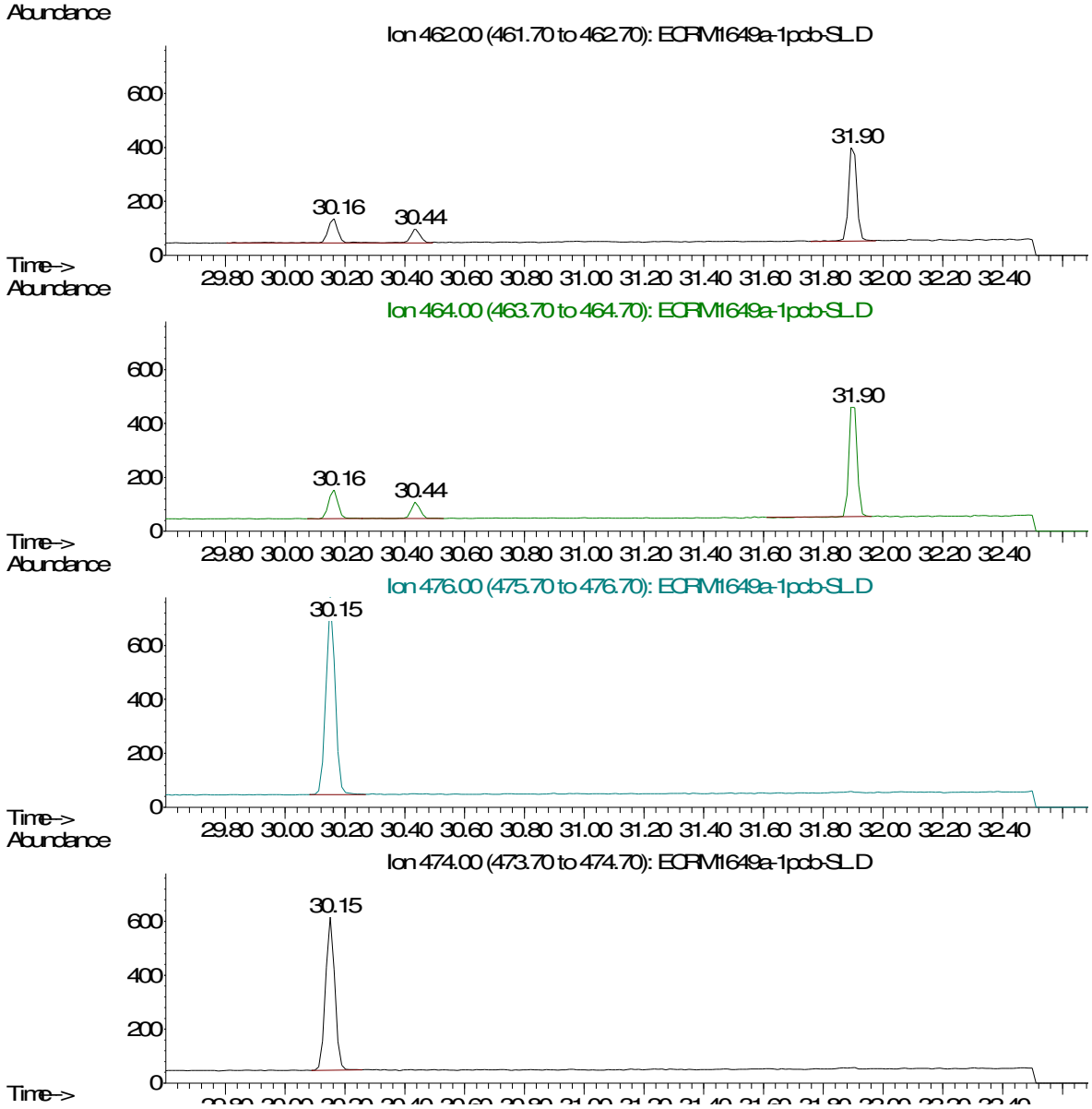


Figure S 23 Chromatogram in selected ion monitoring mode for NonaPCBs of NIST SRM 1649a.

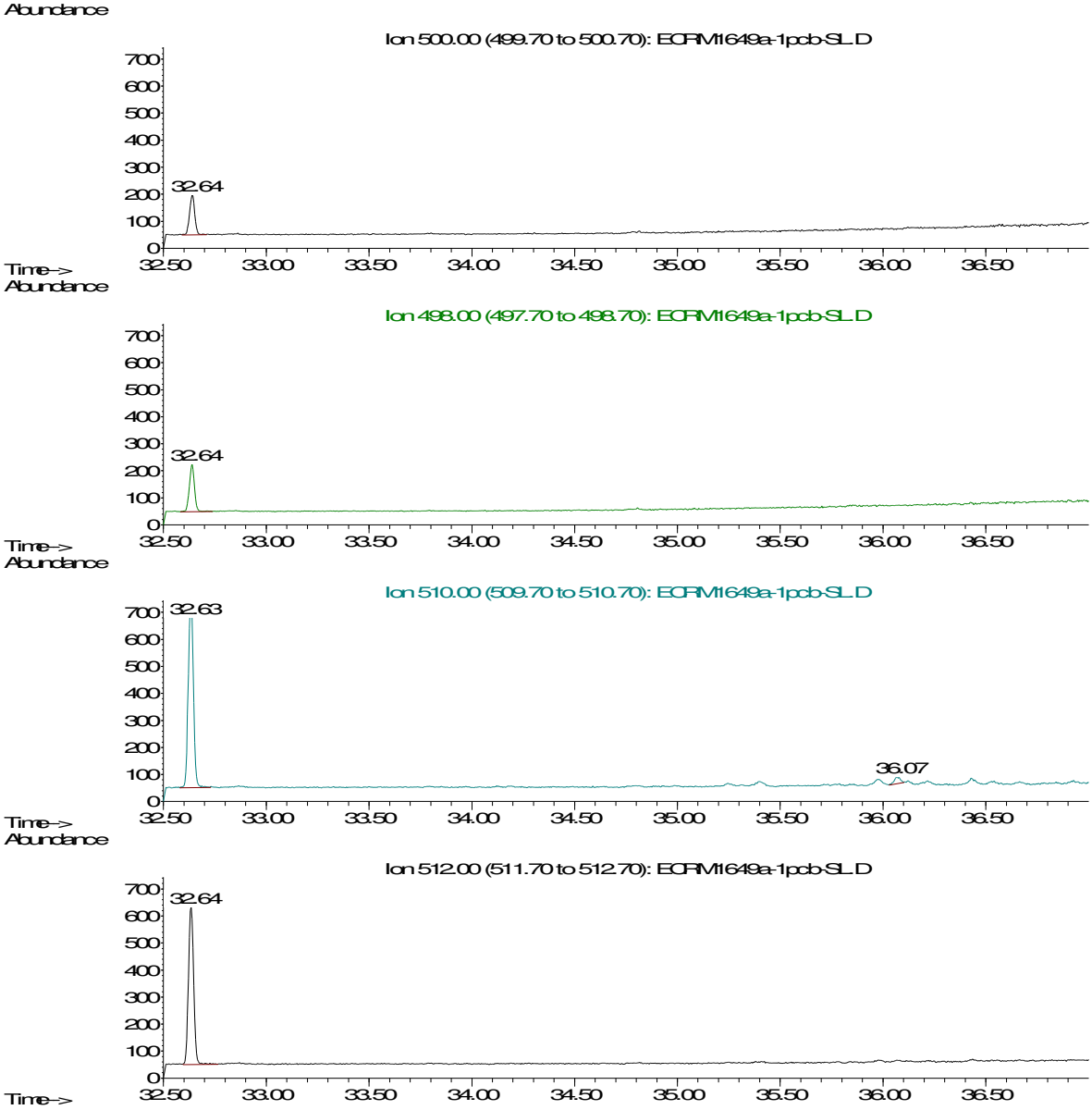


Figure S 24 Chromatogram in selected ion monitoring mode for DecaPCB of NIST SRM 1649a.

References

NIST, 2007. National Institute of Standards and Technology (2007) Certificate of Analysis; Standard Reference Material 1649a Urban Dust

3. Polychlorinated biphenyls, polychlorinated dibenzo-p-dioxins and dibenzofurans in street dust of North Rhine-Westphalia, Germany

Redrafted from "Klees, M.; Hiester, E.; Bruckmann, P.; Molt, K.; Schmidt, T.C. Polychlorinated biphenyls and polychlorinated dibenzo-p-dioxins and dibenzofurans in street dust of North-Rhine Westphalia, Germany. *Sci. Total Environ.* **2015**, *511*, 72-81."

3.1 Introduction

Street dust as a complex environmental matrix refers to the load of deposited dust on an imperviously paved surface. Furthermore, the term street dust refers not only to dust that exists on surfaces next to a road, but also to dust that accumulates on paved surfaces at industrial sites originating from processes taking place at those premises [Klees et al., 2013]. A primary benefit of using street dust as sampling matrix is its easy availability, its ability to reflect various contaminations originating from multiple sources and its potential as an indicator for pollutant levels of inorganic or organic compounds for the assessment of their environmental fate and pathways [Yang and Baumann, 1996; de Miguel et al., 1997; Loganathan et al., 1997; Irvine and Loganathan, 1998; Zakaria et al., 2002; Leung et al., 2011; Cao et al., 2012; Okorie et al., 2012; Li et al., 2013; Wang et al., 2013]. Furthermore, health risks associated with uptake of contaminated dust may need to be evaluated, in particular at industrial sites. However, so far only a few studies have dealt with the determination of polychlorinated biphenyls (PCBs) and polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDDs/PCDFs) in street dusts [Yang and Baumann, 1996; Irvine and Loganathan, 1998; Leung et al., 2011]. In contrast, more studies are published on indoor house dust samples [Wittsiepe et al., 1997; Harrad et al., 2006; Harrad et al., 2010; Deziel et al., 2012], which is important for health risk assessments after exposure to contaminated indoor dusts. PCBs and PCDDs/PCDFs are highly toxic compounds that belong to the group of persistent organic pollutants (POPs), defined by the Stockholm convention in 2001 [Stockholm Convention on Persistent Organic Pollutants (POPs). Stockholm, 2009]. Those toxic substance classes are known for their persistence in the environment, bioaccumulation

in the fatty tissue of living organisms and the ability to undergo long-range transport. In the last decades, PCBs were synthesized for use in several industrial applications. Due to their chemical and physical properties large quantities of manufactured PCBs were applied as transformer oil, hydraulic fluid or as additives in sealants, paints or plastics. In contrast to PCBs, PCDDs/PCDFs are unintentionally formed byproducts in thermal processes (e.g. waste incineration; metallurgic processes) in the presence of organics and chlorine. Additionally, PCDDs/PCDFs can result as impurities from several organochlorine formulation processes [Fiedler, 1996].

PCBs and PCDDs/PCDFs are initially mostly emitted into the atmosphere before being transferred into other environmental compartments. Investigations about gas-particle partitioning of individual PCDD/PCDF and PCB congeners and homologue groups consistently show that lower chlorinated congeners preferentially stay in the gas phase, while higher chlorinated ones are mostly particle bound [Lohmann et al., 2000; Mandalakis et al., 2002].

The major removal pathway for POPs from the atmosphere to the terrestrial compartment is wet and dry atmospheric deposition [Koester and Hites, 1992]. Once deposited on impervious surfaces pollutants accumulate in the presence of inorganic and/or organic matter. Depending on their individual physical and chemical properties PCBs and PCDDs/PCDFs may also redistribute through volatilization or will be degraded.

After implementing comprehensive regulations to minimize PCB and PCDD/PCDF emissions [Siebzehnte Verordnung, 1990; Regulation 2000/76/EC] the success of these controls can be seen in time trends of PCBs in ambient air showing for example decreasing concentrations in the UK [Schuster et al., 2010a]. Between 2005 and 2009 a slight increase of PCB concentrations in ambient air of the city of Dortmund, a major industrial town in North Rhine-Westphalia, was observed and traced back to improper handling of large PCB contaminated transformers and condensers at a recycling company in the harbour area [Bruckmann et al., 2011; Bruckmann et al., 2013]. At that site, monitoring programs with vegetables, bioindicators, atmospheric deposition and analyses of street dust samples taken on industrial sites finally led to the identification of the mentioned PCB emission source [Bruckmann et al., 2011]. Triggered by the incident in Dortmund a major aim of this study is to show that street dust as easily accessible sampling matrix can more generally be used to trace back such industrial contaminations. To that end, mass concentrations and area concentrations of PCB6, total PCB, dl-PCB toxic equivalents (TEQ) and PCDD/PCDF TEQ

(a definition of the terminologies can be found in section 3.2.5) in street dust samples have been exemplarily measured in order to generate comparison values for the assessment of concentrations of PCBs and PCDDs/PCDFs that are analysed on industrial sites. An analytical method for the determination of PCBs and PCDDs/PCDFs in street dust samples was developed previously and applied in this study [Klees et al. 2013]. In addition, particle-size dependent analysis was performed in order to identify the size ranges of the particles that exhibit the highest concentrations, even if such particles do not necessarily make the largest contribution to the mass of the sample. Furthermore, differences in concentrations with respect to sampling site categories were investigated during this study although with only a limited number of samples. Finally, street dust samples were characterized with regard to PCB and PCDD/PCDF homologue and congener specific patterns.

3.2 Materials and methods

3.2.1 Chemicals and materials

All chemicals were analytical grade and purchased from Merck (Darmstadt,Germany). The solvents for extraction and clean-up were picograde for residue analysis and purchased from LGC Promochem (Wesel, Germany).

Alumina and silica were purchased from MP Biomedicals GmbH (Eschwege, Germany). All 13C12- and native PCB and PCDD/PCDF standards were purchased from Cambridge Isotopes Laboratories (Andover, USA). All pressurized liquid extractions were performed using a Dionex ASE 200 system (Sunnyvale, USA). For the analysis of the indicator PCBs #28, #52, #101, #138, #153, #180 and the dioxin-like PCB congeners #123, #118, #114, #105, #167, #156, #157, #189 a gas chromatograph (GC; model 6890N with an autosampler model 7683) with low resolution mass spectrometer (model 5973N) (all Agilent, Santa Clara, USA) was used. The mono-ortho PCB congeners #77, #81, #126, #169 were analysed using a GC model 6890 Series 2 (Agilent) with a CTC HTX PalPlus autosampler and a high resolution mass spectrometer (model DFS; Thermo Fisher Scientific, Bremen, Germany). Both GCs were equipped with a DB-5 column (J&W) (50 m; 0.20 mm I.D.; 0.11 µm film thickness). Analysis for all 2,3,7,8-PCDD/PCDF and PCDD/PCDF homologue groups was done on the same high resolution mass spectrometer but with another GC column (SP-2331, 60 m; 0.25 mm I.D.; 0.20 µm film thickness from Supelco (Bellefonte, USA).

3.2.2 Sampling sites

Sampling sites were classified into four categories. Namely, samples were taken from rural (R), urban (U), industrially influenced urban (UI) and industrial (I) sampling sites. An overview is given in Table 1. The selection of actual sampling sites was randomly done in accordance to the nature of the surface (almost smooth), to its visible load of dust which can be sampled, to the occurrence of undesired pollution and of course to its match to the sampling site category. The street dust samples were collected from urban sites in Bonn, Cologne, Leverkusen, Essen and Düsseldorf, from rural sampling sites in the Eifel region and from industrially influenced urban sites of North Rhine-Westphalia, Germany. Samples at urban sites were taken in the city centre or in its vicinity of those North Rhine-Westphalian cities (population: > 100.000) having no known PCB or PCDD/PCDF emitting facilities within a distance of 1.5 km to the sampling site. The remote area of the Eifel region is covered mostly by forests, and the absence of potentially PCB or PCDD/PCDF emitting heavy industries makes that region an excellent rural sampling site for obtaining background levels of PCB or PCDD/PCDF in street dusts. Industrially influenced urban areas are typical for the Ruhr area. The densely populated Ruhr area conurbations like Duisburg, Essen and Dortmund are famous for distinct activities in coal mining and steel production in the recent past and some potentially PCB or PCDD/PCDF emitting facilities are still operating. Furthermore, the harbour area of Dortmund is an important transfer site for scrap and new metals. Additional samples from pavements of North Rhine-Westphalian industrial sites were taken during the identification process of a secondary source for PCBs in the harbour area of Dortmund and a survey of industrial facilities where PCB containing materials such as electronic scrap (transformers; capacitors) are recycled in day-to-day business, respectively [Bruckmann et al., 2011; Schwerpunktinspektionsprogramm PCB, 2012].

3.2.3 Sampling and analytical procedure

Street dust samples were collected after bordering a square meter on the ground at a sampling site and sampling was performed as described previously [Klees et al., 2013]. It could be demonstrated that the sampling method applied here enables quantitative sampling of street dust. Furthermore, it was shown that mass recoveries in spiking experiments of a dust surrogate on asphalt and concrete were in general greater than 90% [Klees et al., 2013]. The deposited material was sampled quantitatively using a natural-bristled hand brush and a stainless steel scoop for transferring the material into glass bottles (precleaned by laboratory dish washer; heated at 400 °C over night). The samples were taken either directly from the

street or, where sampling was not possible due to traffic or other circumstances, from the pedestrian or bicycle path beside the street. If the dust loading from one square meter seemed to be insufficient for analysis, the sampling area was enlarged. Actual sampling areas and sampling data are given in **Table 7** and **Table 8**. Sampling was performed during dry weather conditions with temperatures ranging between 7.7 °C (09.03.2011) and 13.8 °C (26.05.2011). After air drying in clean laboratory conditions each sample was particle size fractionated. Following soil analytical methods [Bundes-Bodenschutz- und Altlastenverordnung, 1990], coarse grains >2000 µm were separated and not analysed. Street dust particles <2000 µm were sieved into particle size classes from <2000 µm to >1000 µm, <1000 µm to >500 µm, <500 µm to >250 µm, <250 µm to >125 µm, <125 µm to >63 µm and <63 µm using stainless steel sieves (Retsch, Haan, Germany). Each fraction was analysed for PCBs and PCDDs/PCDFs separately. Analyses for the considered 18 individual PCBs, namely PCB #28, #52, #101, #138, #153, #180, #77, #81, #126, #169, #123, #114, #118, #105, #167, #156, #157, #189, all 17 2,3,7,8 chlorine substituted PCDD/PCDF congeners, PCB (tri- to decachlorobiphenyl) and PCDD/PCDF (tetra- to octachlorine substituted) homologue groups in street dusts were performed after pressurized solvent extraction and gas chromatography coupled to mass spectrometry and met the criteria for determination as described in DIN EN 1948 2-4 [Stationary source emissions, 2006a; Stationary source emissions, 2006b; Stationary source emissions, 2010]. Detailed information on the analytical procedure can be found elsewhere [Klees et al., 2013].

3.2.4 Quality assurance

For the analysis of individual street dust fractions recoveries of single $^{13}C_{12}$-PCB- and PCDD/PCDF quantification standards were monitored. For example, the average recoveries were ranging from 78±19% for $^{13}C_{12}$-PCB #28 (n=106) and 41±12% for $^{13}C_{12}$-PCB #209 (n=106). Calculated average recoveries for $^{13}C_{12}$-2,3,7,8-TCDD were 87±14% (n=103) and for $^{13}C_{12}$-OCDF 70±58% (n=103), respectively. Even though the recoveries for OCDF differed considerably, the use of isotope dilution analysis for the quantification of native OCDF in street dust sample fractions safeguards its correct determination.

The limit of detection (LOD) was defined as the average method blank value concentration for each congener or homologue plus three times its standard deviation. Alternatively, for congeners or homologues not detected during single method blank analyses the LOD was established to be three times the baseline noise. In order to calculate summary statistics, non-detected concentrations were replaced with half the method detection limit for the calculation

of the total concentration of the particle fraction <2000 µm as is routinely done in environmental analysis. However, one should note that summary statistics can be affected by the substitution of LODs with half of their values. Therefore, alternative procedures such as the Kaplan-Meier method for the handling of LODs in summary statistic calculation have been suggested [Antweiler et al. 2008; Helsel et al. 2009]. We have compared both approaches exemplarily and corroborated that our major findings are not affected by use of either procedure. Thus, we maintained the half of LOD approach in order to keep consistency with previously published data. For PCB method blank analysis (n=7) each individual PCB congener could be detected at least in one single analysis. In particular, the indicator PCBs (PCB #28, #52, #101, #138, #153, #180) were detected in all method blanks. In general, LODs were ranging from 0.0041 (PCB #169) to 7.9 (PCB #138) ng/sample. For PCDD/PCDF method blank analysis (n=6) only 1,2,3,4,6,7,8-HpCDD, OCDD, 1,2,3,4,6,7,8-HpCDF and OCDF could be detected at least in one single analysis. Here, resulting LODs were ranging from 4.3 (1,2,3,4,6,7,8-HpCDF) to 63 (OCDD) pg/sample. Congener and homologue specific blank values and LODs for PCBs and PCDDs/PCDFs are listed in the Supporting Information. Concentrations exceeding the LOD were not blank corrected.

3.2.5 Data presentation and statistical analysis

Results for the occurrence of PCB6 in street dust samples are expressed as the sum of the six indicator PCBs (#28, #52, #101, #138, #153, #180) [Ballschmiter and Zell, 1980]. This approach is in accordance to the Guidance on the Global Monitoring Plan for Persistent Organic Pollutants [UNEP, 2007]. Total PCB is defined as PCB6 times five in several pertinent regulations such as the ones for the calculation of total PCB in petroleum products and used oils [Petroleum products and used oils, 2001] and for the calculation of total PCB in waste materials [Regulation 850/2004/EC]. Therefore, this approach was adopted here. Nevertheless one should note that if this approach is applied for the calculation of total PCB an overestimation of total PCB can occur, which can be seen from the correlation of the sum of tri- to decachlorobiphenyls and PCB6*5 (**Figure S 29**).

In addition, dioxin-like PCB (dl-PCB) and PCDD/PCDF results in street dust samples are expressed according to van den Bergh et al. as toxic equivalents [van der Berg et al., 2006].

PCB homologue patterns are presented as the mass fraction of each homologue to the total mass of tri- to decachlorobiphenyls.

PCDD/PCDF homologue patterns are presented as the mass fraction of each homologue to the total mass of tetra- to octachlorodibenzodioxins and -furans. In addition, standard deviations of mass fractions of each individual homologue are indicated as error bars. Homologue concentrations below the LOD were taken into account with half of the LOD concentration for the calculation of an average homologue concentration.

PCB6, total PCB, dl-PCB TEQ and PCDD/PCDF TEQ area concentrations for particles <2000 µm were calculated as the sum of the area concentrations of each particle size fraction. The area concentration A_C in µg/m^2 for PCB6, in ng/m^2 for dl-PCB and in pg/m^2 for PCDD/PCDF for each particle size fraction was calculated as

$$A_C = c_m \frac{m_s}{A} \quad (1)$$

where c_m in µg/kg (PCB6) or ng/kg (dl-PCB, PCDD/PCDF) describes the mass concentration, ms in kg is the sampled mass per particle size fraction and A in m^2 describes the sampling area. Congeners that were detected below the LOD during the analysis of individual mass concentrations per fraction were included with half of their LOD values to account for the calculation of the area concentration <2000 µm. Previous investigations concerning the completeness of dust sampling safeguard the correct determination of the area concentration [Klees et al., 2013].

Statistical computations were performed with R 3.0.2 software [R, 2013]. Tests for normality within a group of data were performed with the Shapiro-Wilk test. Averages respectively variances between groups were compared with one- or two-sided t-tests respectively F-tests. In all cases a test was regarded as significant if $p \leq 0.05$.

A central point in this study was the identification of single hot spots with extremely high concentrations compared to the rest of the samples within a certain group. The strategy we used for finding such “hot spots” was a stepwise removal of the highest concentration values until the rest of the data proved to be normally distributed. This is in accordance to the approach as described by van der Loo et al., (2010a and 2010b) which assumes that the bulk of the data within a certain group are normally distributed and looks for extreme values which are unlikely to come from the bulk distribution.

Linear regression was used to individually analyse the relationships between PCB6, PCDD/PCDF TEQs and dl-PCB TEQs concentration and average particle size per fraction.

3.3 Results and discussion

3.3.1 Concentration of PCB and PCDD/PCDF in street dust

PCB6 and TEQ for dl-PCB and PCDD/PCDF concentrations for particle size fractions <2000 µm are calculated taking into account the mass fraction for each particle size range and its individual PCB and PCDD/PCDF concentration, respectively. Those results are summarized in **Table 7** and **Table 8**. This table shows the results of the analysis of street dust samples from two rural (R), six urban (U), eight industrially influenced urban (UI) and five industrial areas (I).

Samples from industrial areas (I)

Samples I4 and I5 were taken at indoor working areas on industrial sites and show PCB6 concentrations of 13000 µg/kg and 2000 µg/kg. PCB6 concentrations of samples I1-I3, which were taken outdoors ranged from 710 µg/kg – 8400 µg/kg. Regulation EC 850/2004 sets a threshold value for total PCB (defined as PCB6 times five) concentration of 50 mg/kg for waste materials, corresponding to 10000 µg/kg PCB6. This threshold value was adopted as action level for remediation activities at industrial sites in a systematic survey of industrial facilities [Schwerpunktinspektionsprogramm PCB, 2012; Regulation 850/2004/EC]. Apart from industrial dust sample I4 the industrial dusts presented here do not exceed this threshold and thus are not classified as polluted. Nevertheless one should note that higher PCB6 concentrations can be found [Bruckmann et al., 2011].

Even if the threshold value for PCB6 set in EC 850/2004 was not exceeded one should be aware of the fact that airborne transport can redistribute such, in the authors' opinion, highly contaminated dusts and deposit them in the neighbourhood of the emission sites. This can cause local high concentrations in areas where no direct contamination sources are obvious. As described below several such "hot spots" were found in our study. In addition the potential volatilization from the dust matrix increases the chances for the long-range transfer of contaminants via the atmosphere into other terrestrial or aquatic compartments. This is the reason why even in rural areas distinct levels of contaminants are observed. Taking into account former findings for the volatilization of semivolatile organic compounds estimated for the transfer from soil to air [Hippelein and McLachlan, 1998; Cousins and Jones, 1998; Hippelein and McLachlan, 2000; Wong and Bidleman, 2011], it can be expected that especially lower chlorinated PCBs may evaporate to the atmosphere.

Dl-PCB TEQ concentrations for industrial dust samples ranged between 75-830 ng/kg and PCDD/PCDF TEQs between 1.3-44 ng/kg with an additional extremely high value of 2400 ng/kg for a transformer disassembling area (I5). This concentration was even higher than in dust samples reported from industrial premises for e-waste recycling [Leung et al., 2011].

Samples from non-industrial areas (R+U+ I)

Figure 10 shows the overall situation for non-industrial samples. Compared to industrial sites relatively moderate concentration levels were measured. But for a few samples for each of the three compound groups extraordinarily high concentrations were observed indicating hot spots (samples UI2, UI7, UI8, U1, U5). The highest concentration values for PCB6 (190 µg/kg) and dl-PCB TEQ (59 ng/kg) are resulting from sample UI8 which originates from an asphalt path at a garden plot in the Dortmund harbour area in direct vicinity to a site where transformers and condensers containing PCB formulations are recycled [Bruckmann et al., 2011]. Despite the existence of a hot spot the concentration of 190 µg/kg observed for PCB6 in this sample is far below the above mentioned threshold of 10000 µg/kg set in regulation EC 850/2004. PCB formulations used in transformers can contain substantial impurities of PCDDs/PCDFs. Consequently, sample UI8 also represents a hot spot with respect to PCDD/PCDF (18 ng/kg). Interestingly, the PCDD/PCDF concentrations reported for house dusts in proximity to industrial facilities and traffic were at least five times higher as the PCDD/PCDF mean for all non-industrial dusts observed during this study [Wittsiepe et al., 1997; Deziel et al., 2012]. Also Leung et al. reported higher PCDD/PCDF concentrations of up to 76 ng/kg in street dust samples taken in a village near a rather rudimentary e-waste processing site in southeast China with cytotoxicity tests suggesting potential harm to the health of workers and local residents [Leung et al., 2011].

Two other industrially influenced samples from the urban area of Duisburg-Wanheim (UI2, UI7) were identified as additional extreme values with regard to PCDD/PCDF concentration (31 ng/kg and 25 ng/kg). Those sampling spots are in the vicinity of a steel mill and a recycling company, which is specialized on reprocessing of zinc dust, with distances of approximately 1.5 km and 0.5 km to UI2, respectively. It is well known that thermal processes such as metal recycling or metallurgic processes are potential emission sources for PCDDs/PCDFs. The allocation of the steel mill as source for these two hot spots is further supported by the PCDD/PCDF homologue pattern observed for UI2 and UI7 as discussed later in this study.

Also in the case of PCB6 two additional extreme values (160 µg/kg and 130 µg/kg) were found in samples U1 and U5 originating from the city centres of Leverkusen and Essen. Indeed, in such urban city centres population density has been proposed to correlate with elevated PCB levels [Schuster et al., 2010b]. Furthermore, urban areas are permanently subjected to construction works of buildings, roads or public transport infrastructure. PCBs from PCB-containing construction materials may outgas and condensation on street dust particles takes place or particles from abrasion of PCB-containing construction material can be responsible for increased PCB6 concentrations in urban street dusts. For example, very high PCB6 concentrations were detected in elastic sealants from Danish apartments constructed in the early 1970s [Frederiksen et al., 2012].

Table 9 shows the concentration ranges and means for all three compound groups after removing the extreme values corresponding to the hot spots. T-tests showed that the differences between the means of the rural (R), the urban (U) and industrially influenced urban area (UI) are insignificant.

The highest mean PCB6 concentration (50.5 µg/kg) was found in the urban area (U). This value again is far below the above mentioned threshold of 10000 µg/kg. The mean PCDD/PCDF concentration was 2.4 ng/kg in the rural (R) and about 4.3 ng/kg in the urban areas (U + UI). These concentration levels of rural and urban sampling sites are in agreement with dust samples analysed at a reference site with no nearby emission source in Southeast China [Leung et al., 2011], where a PCDD/PCDF TEQ concentration of 3.47 ng/kg had been determined. PCDD/PCDF concentrations in rural areas were attributed to meteorological effects and long-range transport of particle-bound PCDD/PCDF, but other non-industrial primary PCDD/PCDF sources, like domestic solid fuel combustion, accidental fires or motor vehicle emissions play an important role for densely populated regions such as city centres [Quaß et al., 2004].

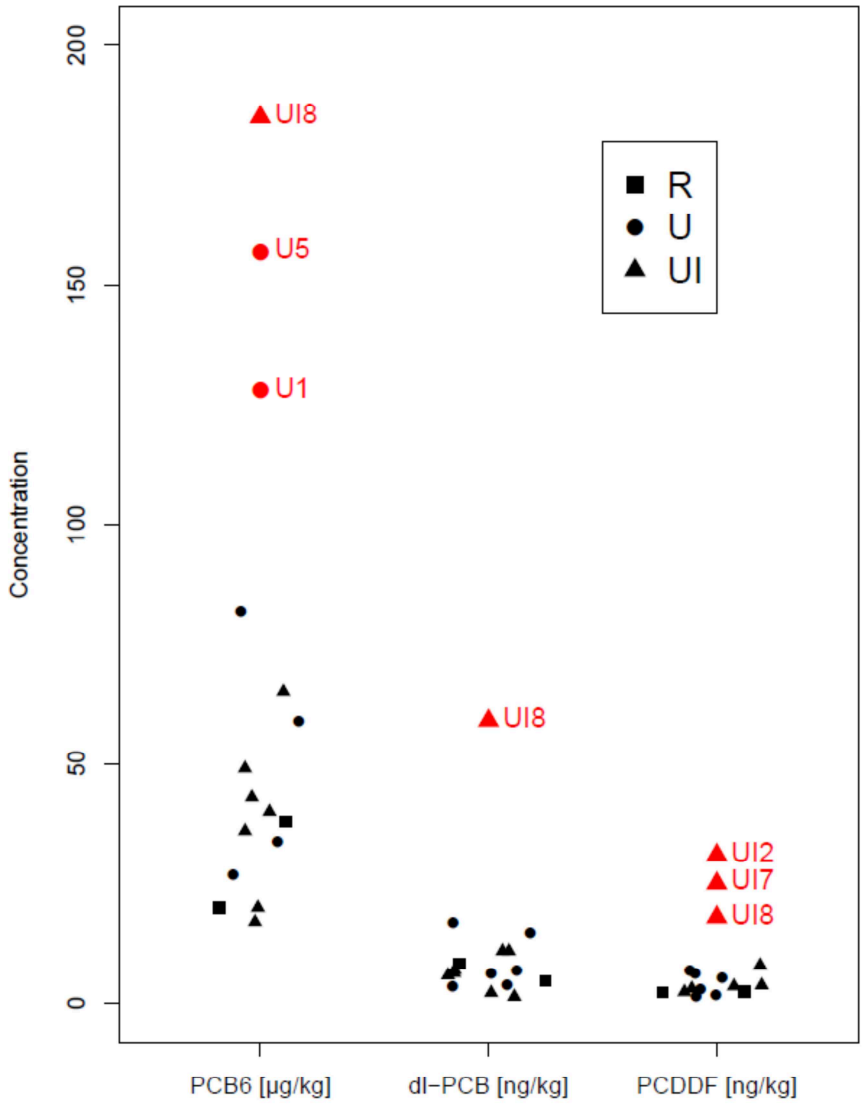


Figure 10 Concentration levels of PCB6, dl-PCB TEQs and PCDD/PCDF TEQs in street dusts analysed during this study. Rural (square), urban (circle) and industrially influenced street dusts (triangle) are marked. Identified "hot spots" are highlighted in red.

Particular emphasis should be placed on dl-PCBs. To our knowledge similar analyses of dl-PCB concentrations in street dusts have not been performed before. In **Table 7** and **Table 8** we therefore present dl-PCB TEQs and calculate their relative contribution to total TEQ (dl-PCB TEQ + PCDD/PCDF TEQ). Contributions of dl-PCB and PCDD/PCDF TEQ varied among the sampling sites. Dl-PCB TEQs were predominant in all but three investigated

samples with a fraction of up to 77% in sample UI8. Summarized for all samples dl-PCB contributions were calculated to 58±18 % of total TEQ. A predominant PCDD/PCDF TEQ contribution to total TEQ was only observed for three sampling locations next to potential PCDD/PCDF emission sources. At these sampling sites (UI2, UI6, UI7) contributions greater than 70% PCDD/PCDF TEQ to total TEQ were determined. For ambient air and atmospheric deposition samples at urban background sites dl-PCB TEQ contributions of about 30% to total TEQ have been reported [Bruckmann et al., 2013]. Investigations of soil samples from North Rhine-Westphalia showed average dl-PCB contributions of about 18% and average PCDD/PCDF TEQ contributions of about 82% to total TEQ (LANUV internal communication; **Table S 29**). The higher contributions of dl-PCB TEQ in street dust samples investigated during this study can stem from a better retention of dl-PCBs in street dust in comparison to PCDDs/PCDFs.

Altogether the results discussed in this section indicate that street dusts have promising potential as ubiquitously available passive sampling matrix for the screening of PCBs and PCDDs/PCDFs.

Table 7 Overview of results for street dust samples: Information of sampling date, sampling site and category, sampling mass and area are given. Furthermore, PCB6, total PCB, PCDD/PCDF TEQ and dl-PCB TEQ mass and area concentrations are depicted for each individual sampling site.

Number	Date (day.month.year)	Description	Sampled area	Sampled mass (<2000 µm)	PCB6[b] (<2000 µm)		Total PCB[c] (<2000 µm)		dl-PCB TEQ[a] (< 2000 µm)		PCDD/PCDF TEQ[a] (< 2000 µm)		Total TEQ (dl-PCB TEQ + PCDD/PCDF TEQ) ng/kg	Contribution to total TEQ	
			m^2	g	µg/kg	µg/m^2	µg/kg	µg/m^2	ng/kg	ng/m^2	ng/kg	pg/m^2		dl-PCB TEQ contribution (%)	PCDD/PCDF TEQ contribution (%)
UI1	09.03.2011	Duisburg-Buchholz Böhmerstr.	1	120	20	2.5	100	12	2.2	0.23	3.1	370	5.3	42	58
UI2	09.03.2011	Duisburg-Wanheim Ehinger Str.	2	14.1	65	0.46	330	2.3	11	0.072	31	220	42	26	74
UI3	09.03.2011	Duisburg-Wanheim Kaiserswertherstr.	2	26.1	40	0.52	200	2.6	7.0	0.080	8.0	110	15	47	53
UI4	09.03.2011	Essen-Vogelheim Hafenstr.	1	527	43	22	210	112	6.4	2.6	3.8	2000	10.2	63	37
UI5	09.03.2011	Dortmund-Eving Burgweg	2	53.1	31	0.94	150	4.7	5.9	0.12	2.4	63	8.3	71	29
UI6	02.05.2011	Duisburg-Marxloh	5	12.0	17	0.040	85	0.20	1.4	0.0038	3.6	8.7	5.0	28	72
UI7	02.05.2011	Duisburg-Wanheim	3	37.8	46	0.61	230	3.1	11	0.12	25	320	36	31	69
UI8	02.05.2011	Dortmund harbour area; garden plot	2	11.8	190	1.1	950	5.5	59	0.31	18	100	77	77	23
U1	30.03.2011	Leverkusen-Center Dhünnstr.	2	7.9	130	0.43	650	2.1	17	0.043	6.9	24	23.9	71	29
U2	30.03.2011	Düsseldorf-Center Bendemannstr.	2	19.8	59	0.58	290	2.9	6.5	0.065	3.1	32	9.6	68	32
U3	30.03.2011	Köln-Deutz Brügelmannstr.	2	62.9	27	0.85	140	4.3	3.7	0.12	1.7	55	5.4	69	31

Table 8 Overview of results for street dust samples: Information of sampling date, sampling site and category, sampling mass and area are given. Furthermore, PCB6, total PCB, PCDD/PCDF TEQ and dl-PCB TEQ mass and area concentrations are depicted for each individual sampling site.

Number	Date (day.month.year)	Description	Sampled area	Sampled mass (<2000 µm)	PCB6[b] (<2000 µm)		Total PCB[c] (<2000 µm)		dl-PCB TEQ[a] (< 2000 µm)		PCDD/PCDF TEQ[a] (< 2000 µm)		Total TEQ (dl-PCB TEQ + PCDD/PCDF TEQ)	Contribution to total TEQ	
			m^2	g	µg/kg		µg/m^2		µg/kg		µg/m^2		ng/kg	ng/m^2	
U4	30.03.2011	Köln-Center Heumarkt	2	11.2	82	0.46	410	2.3	7.1	0.039	5.6	98	12.7	56	44
U5	30.03.2011	Essen-Center Gerswidastr.	2	28.3	160	0.27	800	1.3	15	0.030	6.3	16	21.3	70	30
U6	30.03.2011	Bonn-Center Am Marthashof	3	15.7	31	1.5	160	7.4	3.9	0.14	2.0	60	5.9	66	34
R1	26.05.2011	Simmerath / Waldsiedlung	4	22.5	38	0.21	190	1.1	8.3	0.047	2.5	14	10.8	77	23
R2	26.05.2011	Roettgen / Schwerzfeldstr.	3	24.8	20	0.17	100	0.83	4.7	0.039	2.3	19	7.0	67	33
I1	27.04.2010	Industrial site; compactor area	-	110	710	75	3600	380	75	7.9	11	1200	-		-
I2	27.04.2010	Industrial site; shredder area	-	100	1700	173	8500	860	210	23	17	1800	-		-
I3	27.04.2010	Industrial site; junk yard	-	-	8400	-	42000	-	330	-	44	-	-		-
I4	07.06.2010	Industrial site; factory work floor	-	-	12600	-	63000	-	830	-	1.3	-	-		-
I5	24.01.2011	Industrial site; transformator disassembling area	-	-	2000	-	10000	-	-	-	2400	-	-		-

Table 9 Ranges, means and standard errors of means and medians for the non-industrial samples after excluding the hot spots.

	PCB6 [µg/kg]	dl-PCB TEQ [ng/kg]	PCDD/PCDF TEQ [ng/kg]
Rural area (R)			
Number of samples	2	2	2
Range	20-38	4.7-8.3	2.3-2.5
Mean ± standard error	29±9	6.5±1.8	2.4±0.1
Median	29	6.5	2.4
Urban area (U)			
Number of samples	4	6	6
Range	27-82	3.7-17	1.7-6.9
Mean ± standard error	50.5±12.5	8.9±2.3	4.3±0.9
Median	45	6.8	4.4
Industrially influenced urban area (UI)			
Number of samples	7	7	5
Range	17-65	1.4-11	2.4-8.0
Mean ± standard error	38.5±6.3	6.4±1.4	4.2±1.0
Median	40	6.4	3.6
Overall (R+U+UI)			
Number of samples	13	15	13
Range	17-82	1.4-17	2.4-8.0
Mean ± standard error	40.8±5.3	7.4±1.1	3.9±0.6
Median	39	6.5	3.1

3.3.2 Area concentration of PCB and PCDD/PCDF in street dust

Results for PCB6, total PCB, dl-PCB TEQ and PCDD/PCDF TEQ at each sampling site are shown in **Table 7** and **Table 8**. PCB6 area concentrations vary strongly between 0.040 µg/m^2 for UI6 and 22 µg/m^2 for UI5. Dl-PCB TEQ area concentrations ranged from 0.0038 ng/m^2 for UI6 and 2.6 ng/m^2 for UI5. Average and median concentration were calculated to 0.25 ng/m^2 and 0.076 ng/m^2, respectively. A maximum PCDD/PCDF area concentration of 2000 pg/m^2 (UI5) and a lowest PCDD/PCDF area TEQ concentration of 8.7 pg/m^2 (UI6), average PCDD/PCDF TEQ area concentrations of 220 pg/m^2 and median PCDD/PCDF TEQ concentrations of 61 pg/m^2 were analysed throughout all non-industrial dusts investigated. Regarding the sampled dust masses per square meter in combination with the mass concentrations for dust UI5 and UI6, the conclusion is obvious that area loadings are massively dependent on the amount of dust deposited at the sampling site. The amount of street dust sampled at Essen-Vogelheim is exceeding “regular” sample amounts per square meter in this study by far. One might assume that here dumping of rubble or the like occurred suggesting that illegal dumping of PCB containing materials along the roadside can cause high area burdens and facilitates the distribution of contaminated dusts by meteorological effects.

3.3.3 Particle size related concentrations of PCBs and PCDDs/PCDFs in street dust

For the evaluation of particle sizes exhibiting highest concentrations of PCBs and PCDDs/PCDFs in street dusts, samples were sieved into six particle size fractions as described in the experimental section and were individually analysed for their contaminant concentrations. Corresponding data of PCB6, PCDD/PCDF TEQ and dl-PCB TEQ are shown in Table S21. For some particle size fractions no concentration value could be determined. In these fractions concentrations did not exceed the LOD or the particle size fraction was too small during sampling.

The highest PCB6 concentration of 290 µg/kg was observed for the particle size fraction 500 to 1000 µm of non-industrial sample U6, while sample UI8 had the second and third highest concentration with values of 270 µg/kg and 240 µg/kg (63 to 125 µm and <63 µm), respectively. However, a noticeable distribution of PCB6 concentration with respect to particle size fraction in all investigated non-industrial dusts shows that 50% of the highest PCB burdens were found for the smallest particle size fraction of all samples (<63 µm). In

19% of all investigated samples the highest total PCB concentration was found in the particle size fraction 125 to 250 µm, whereas in 12.5% of all cases particle size fractions 500 to 1000 µm and 63 to 125 µm hold highest total PCB concentrations and only 6.3% was found in particle size fraction 250 to 500 µm, respectively. This observed distribution of highest concentrations correlated to predominantly small particle size fractions has already been observed for other organic and inorganic compounds [Wang et al., 2013] and corroborates Cao et al.'s conclusion for human exposure risk assessment that particle sizes >250 µm should not be considered for analysis [Cao et al., 2012]. The trend towards higher PCB6 concentrations in smaller particle size fractions was not observed in industrial dusts (Table S21; I1-I2). Furthermore, concentrations of PCB6 in each individual fraction are elevated compared to non-industrial dusts. The random formation of PCB6 polluted particles during industrial processes in combination with dispersion of this emitted polluted material may cause deviations from the correlation of decreasing concentrations with an increase in particle size observed in non-industrial street dust samples. However, the finer particles (<100 µm) of industrial dusts, having the ability to be spread by drifting, are already loaded with PCBs in concentrations high enough to cause elevated concentrations in other terrestrial or aquatic compartments.

Among different particle size fractions, PCB6 concentrations may differ by a factor of 2 to 5. For routine analysis of street dust samples in environmental monitoring this variance demonstrates that street dust sample fractions <2000 µm have to be ground if no particle size depending concentration analysis is desired in order to provide sufficient homogeneity for the analysis. If the analyses of street dust shall be focused on human exposure assessment particle sizes <250 µm should be sieved and analysed according to Cao et al. (2012). In addition, for data comparison purposes analogous particle size fractions have to be checked against each other. For example, detected PCB6 concentrations for particle sizes <250 µm calculated from street dust data analysed by Irvine et al. (1998) were ranging from 90 µg/kg to 984 µg/kg, which is comparable to the values presented here. In another street dust study PCB6 concentrations for particle sizes <100 µm ranged from 190 µg/kg to 3600 µg/kg [Yang and Baumann, 1996]. These values generated 20 years ago were clearly higher demonstrating an overall decreasing trend of PCB concentrations in street dusts from Germany.

The inverse correlation of contaminant concentration and particle size observed for PCB6 is even more apparent for PCDD/PCDF TEQ and dl-PCB TEQs in the street dust sample fractions (**Figure 11**). Among different particle size fractions, PCDD/PCDF TEQ

concentrations differ by a factor of up to 20. About 70% of the highest burdens of dl-PCB TEQ and PCDD/PCDF TEQ were found in the smallest particle size fraction. Highest PCDD/PCDF TEQs reached concentrations of up to 66 ng/kg in sample UI2 (<63 µm), whereas the highest dl-PCB TEQ burden of 90 ng/kg was observed in sample UI8 (<63 µm). Kaupp et al. already documented that PCDDs/PCDFs are enriched in atmospheric particulate matter, however in particle diameters by far smaller than those regarded here for street dust samples [Kaupp et al., 1994].

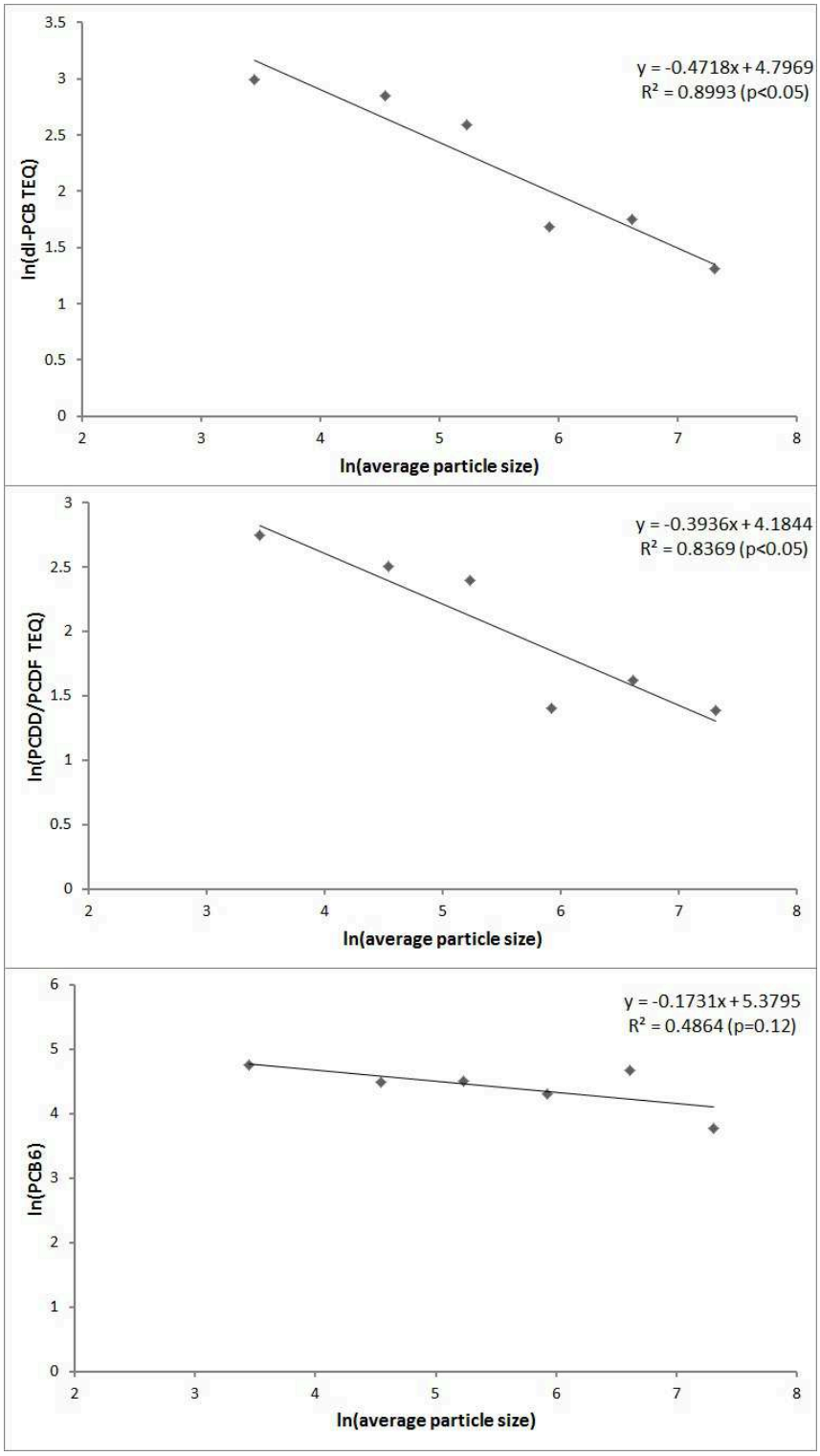


Figure 11 Correlation of logarithmic average dl-PCB TEQ, PCDD/PCDF TEQ and PCB6 concentration in non-industrial street dusts vs. logarithmic average particle size per fraction. Linear regression model equation, correlation coefficient and p-value are additionally shown.

3.3.4 Homologue and congener patterns of PCB and PCDD/PCDF in street dust samples

3.3.4.1 PCBs

The average percentage contribution of the homologuesrelated to their sampling site category is shown in **Figure 12**. Standard errors of mean of each homologue within a sampling site category are indicated as error bars. Differences among homologue profiles in the four sampling site categories can be seen. The homologue profiles for rural and urban areas are characterized by maximum concentrations of hexachlorobiphenyls. Homologue patterns of industrial sites indicate a shift towards lower chlorinated biphenyls with tetrachlorobiphenyls dominating. Breivik et al. (2002) reported that 70% of the estimated total global production of commercial PCB formulations were attributed to lower chlorinated PCBs (tri-, tetra- and pentachlorobiphenyls). However, the large standard deviations for individual homologues reveal that the pattern may be dependent on the PCB contaminated raw material used for the individual processes at the industrial sites and the commercial PCB formulation applied to the raw material. Homologue patterns for industrially influenced urban areas are dominated by hexachlorobiphenyls, similar to urban and rural samples. Elevated concentrations of tetra- and pentachlorinated biphenyls seem to be the result of an overlay with the still significant industrial pattern.

The yearly average homologue patterns of atmospheric deposition and ambient air in Duisburg-Wanheim are exemplarily shown in **Figure S 25** and **Figure S 26**. The homologue patterns of rural and urban street dusts are similar to homologue patterns of atmospheric deposition. PCBs in urban, rural and industrially influenced urban area street dust samples can therefore be attributed to the deposition of PCB loaded particles as major pathway.

Due to the combination of the global production of mostly lower chlorinated commercial PCB formulations and their higher volatility, homologue patterns of ambient air samples are dominated by tetrachlorobiphenyls just as the homologue pattern for dust samples on industrial sites. The similarity between the homologue pattern of industrial dust samples and the pattern of ambient air indicates dusts with origin from industrial sites as a secondary source of lower chlorinated PCBs to the atmosphere. Monitoring studies of PCBs in ambient air noted faster decay rates for these lower chlorinated PCBs (e.g. PCB #28; #52) than for higher chlorinated PCBs (e.g. PCB #138; #153) resulting in almost constant concentrations

for higher chlorinated PCBs and in decreasing concentrations of lower chlorinated PCBs since monitoring was started in the late 1980's [Bruckmann et al., 2013].

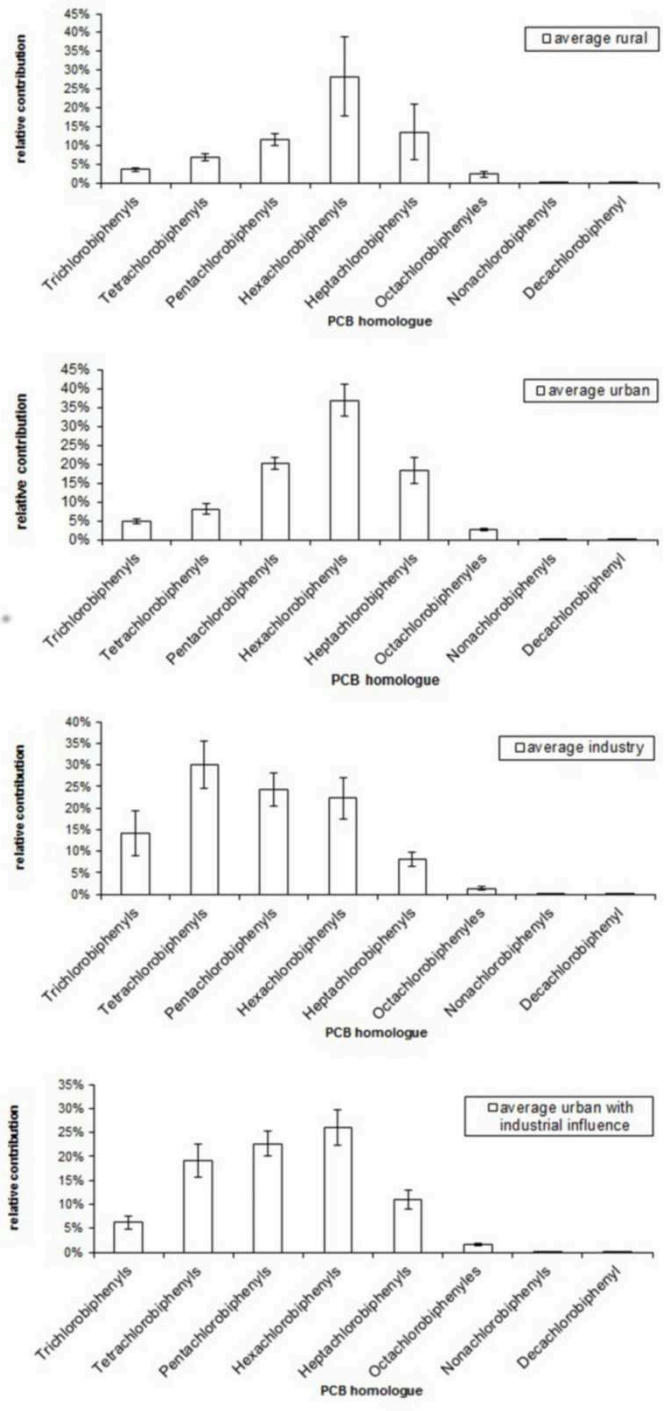


Figure 12 PCB homologue patterns of street dust samples according to sampling site category. The average homologue pattern for each sampling category is calculated from the homologue pattern of each sample. Individual homologue patterns are expressed as the relative percentage of each homologue to the sum of tri- to decachlorobiphenyl. Error bars are expressed as standard error of means.

3.3.4.2 PCDD/PCDFs

For non-industrial street dust samples investigated during this study a consistent homologue pattern has been observed (**Figure 13**). In the majority of investigated street dust samples OCDD is dominating the pattern. This supports previous findings of Leung et al. (2011). Investigations of deposition and urban soil samples by Ogura et al. (2001) have shown that the homologue profiles of those urban matrices are often dominated by OCDD, too. In urban street dust samples the dominance of OCDD is most pronounced. This has also been reported for urban ambient air samples in England [Dyke et al., 1997]. For urban street dust samples an OCDD/Total PCDD/PCDF ratio of 0.44±0.12 and a PCDF/PCDD ratio of 0.62±0.31 have been observed in this study. Higher chlorinated PCDDs/PCDFs are known to distribute preferably bound to particles in ambient air. Thus, the concentration of particulate matter can be of major importance. Wet and dry deposition of these particles contribute to the specific homologue distribution in street dust samples. Higher chlorinated PCDDs/PCDFs, especially OCDD, could also be enriched over time in urban street dust samples. Ogura et al. (2001) attributed the dominance of OCDD in the homologue profile to its high chemical inertness to degradation processes.

In areas with nearby sintering processes or thermal metal recycling processes homologue patterns of urban street dust samples with industrial influence and deposition can be similar. The homologue patterns of these street dusts (UI2, UI7) (**Figure 13**) and deposition samples (**Figure S 25**) are obviously dominated by the homologue pattern characteristic for the local emission source in the vicinity. This supports the identification of the corresponding extreme concentration values as hot spots. The PCDD/PCDF, especially PCDF, homologue profiles of sample UI2 and sample UI7 are similar to that of a filter dust of a sintering plant (**Figure 13**). This observation for the PCDD/PCDF homologue pattern was unique for the samples UI2 and UI7 and demonstrates the usefulness of analysing homologue patterns in street dust samples as an additional tool in the allocation of possible emission sources.

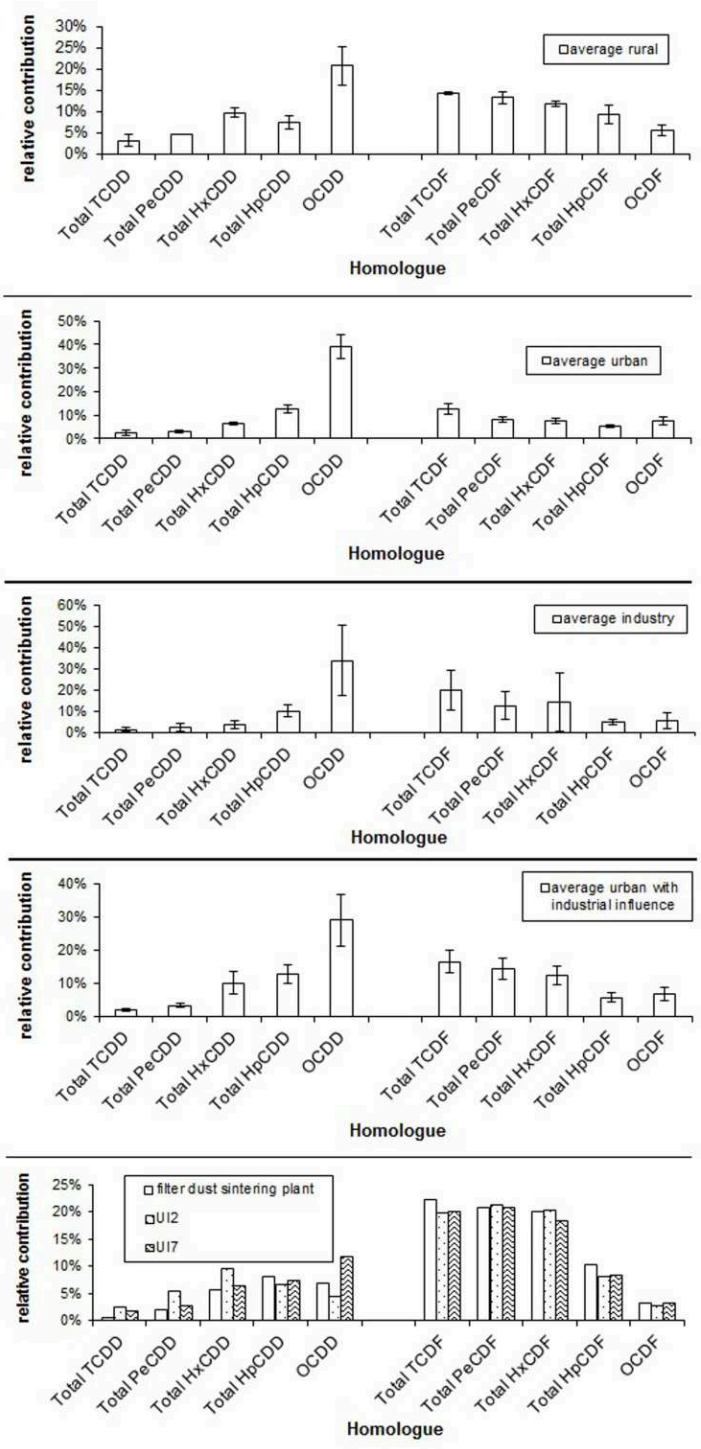


Figure 13 Average PCDD/PCDF homologue patterns of street dust samples according to sampling site category except UI2 and UI7 (upper part). Homologue pattern of UI2 (masoned) and UI7 (checkerboard) and of a filter dust originating from a sintering plant (blank) in the direct vicinity to sampling site UI2 and UI7 (lower part). The average homologue pattern for each sampling category is calculated from the individual homologue pattern of each sample. Individual homologue patterns are expressed as the relative percentage of each homologue to total PCDDs/PCDFs. Error bars are expressed as standard error of means.

3.3.4.3 Congener-specific characterization of PCBs and PCDD/PCDFs in street dust sample

In almost all investigated samples PCB #138 has shown the highest concentration. Similarly, Yang and Baumann (1996) and Irvine and Loganathan (1998) published findings for PCB #138 to be the most abundant congener in street dust samples. Exceptions are found for samples dominated by lower chlorinated biphenyls such as samples of industrial origin (e.g., I2). Here, PCB #28 was found in highest concentration. As has been discussed above for dust samples taken on industrial sites, fresh PCB emission sources, like commercial PCB formulations, can be dominated by lower chlorinated biphenyls. In this study for the group of mono-ortho PCBs a consistent and unchanging contribution has been observed. PCB #118 was found in highest, PCB #114 and #189 in lowest concentration, respectively. Furthermore, for the non-ortho PCBs about 70% are contributed by PCB #77. As shown by Martinez et al. (2000) other environmental matrices influenced by atmospheric deposition such as vegetation samples or soil indicate similar contributions of PCB #77. It is interesting to note that especially the PCB classified as most toxic, PCB #126, shows a different contribution to total non-ortho PCBs associated to sampling site category in the present study. Moreover, the contribution of PCB #126 and PCB #169 to total non-ortho PCBs analysed increases with the distance to a potential emission source (**Figure S 27**). Rural areas are representing background areas that are free of industrial sources, thus long-range transport has been assumed to be responsible for background concentrations. Sinkkonen and Paasivirta (2000) described how during the transport of PCB loaded particles gas-phase reactions with lower chlorinated PCB, like PCB #77 and PCB #81, promote the decreasing contribution of PCB #77 and PCB #81 to total non-ortho PCB in street dusts.

In addition, congener-specific concentration data of 2,3,7,8 chlorine substituted PCDDs/PCDFs were examined in the present study. PCDD/PCDF congener fingerprint patterns observed in single street dust samples were comparable to each other. Significant changes in their congener patterns could not be observed.

The congener profiles of street dust samples investigated were dominated by 1,2,3,4,6,7,8-HpCDF, 1,2,3,4,6,7,8-HpCDD and OCDD. With regard to the contribution of individual 2,3,7,8 chlorine substituted congeners to PCDD/PCDF TEQ highest average contribution throughout all samples was analysed for 2,3,4,7,8-PeCDF (19±5%), followed by 2,3,4,6,7,8-HxCDF (14±4%), 1,2,3,7,8-PeCDD (13±4%) and 2,3,7,8-TCDD (12±8%). This is in good accordance with the congener contribution observed in a Chinese study [Leung et al., 2011].

There, 2,3,7,8-TCDD, 1,2,3,7,8-PeCDD, 2,3,7,8-TCDF and 2,3,4,7,8-PeCDF accounted for up to 70% of total PCDD/PCDF TEQ.

3.4 Conclusions

This study successfully demonstrated that the analysis of street dust samples involving a simple sampling technique can indicate possible PCB or PCDD/PCDF contamination sources and illustrates the usefulness of street dusts as naturally occurring passive samplers. The investigation of particle size related concentrations of PCBs and PCDDs/PCDFs in street dust confirms that small dust particles have greater potential to cause adverse health effects by being higher loaded with pollutants. By far the highest concentrations were measured in samples from industrial areas with direct emission sources such as recycling facilities for transformers. Relatively moderate concentrations were found in the bulk of street dust samples from non-industrial areas. However, in the vicinity of industrial sites a few of these samples showed exceptionally high concentrations. This is due to the fact that the above mentioned industrial street dusts must be regarded as significant reservoirs and even as secondary sources for the dispersion of persistent organic pollutants, causing transfer and redeposition into their neighbourhood in the form of hot spots. Additionally, analysis and comparison of PCB and PCDD/PCDF homologue patterns facilitates allocation of possible emission sources that are responsible for those hot spots.

3.5 References

Antweiler, R.C.; Taylor, H.E. Evaluation of Statistical Treatments of Left-Censored Environmental Data using Coincident Uncensored Data Sets: I. Summary Statistics. Environ. Sci. Technol. 2008, 42, 3732–3738.

Ballschmiter K.; Zell, M. Analysis of polychlorinated biphenyls (PCB) by glass capillary gas chromatography. Fres. J. Anal. Chem. 1980, 302, 20-31.

Breivik, K.; Sweetman, A.; Pacyna, J.M.; Jones, K.C. Towards a global historical emission inventory for selected PCB congeners — A mass balance approach: 1. Global production and consumption. Sci. Total Environ. 2002, 290, 181–198.

Bruckmann, P.; Hiester, E.; Klees, M.; Radermacher, L. Environmental pollution by polychlorinated biphenyls (PCB) in the harbour region of Dortmund. Gefahrst. Reinhalt. der Luft 2011, 4, 151-158.

Bruckmann, P.; Hiester, E.; Klees, M.; Zetzsch, C. Trends of PCDD/F and PCB concentrations and depositions in ambient air in Northwestern Germany. Chemosphere 2013, 93, 1471-1478.

Bundes-Bodenschutz- und Altlastenverordnung, 12.07.1999.

Cao, Z.G., Yu, G., Chen, Y.-S., Cao, Q.M., Fiedler, H., Deng, S.B., Huang, J., Wang, B. Particle size: A missing factor in risk assessment of human exposure to toxic chemicals in settled indoor dust. Environ. Int. 2012, 49, 24-30.

Cousins, I.T.; Jones, K.C. Air-soil exchange of semi-volatile compounds (SOCs) in the UK; Environ. Pollution 1998, 102, 105-118.

de Miguel, E., Llames, J.F., Chacón, E., Berg, T., Larssen, S., Røyset, O., Vadset, M. Origin and patterns of distribution of trace elements in street dust: Unleaded petrol and urban lead. Atmos. Environ. 1997, 31, 2733-2740.

Deziel, N.C.; Nuckols, J.R.; Colt, J.S.; De Roos, A.J.; Pronk, A.; Gourley, C.; Severson, R.K.; Cozen, W.; Cerhan, J.R.; Hartge, P.; Ward, M.H. Determinants of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans in house dust samples from four areas of the United States. Sci. Total Environ. 2012, 433, 516–522.

Dyke, P.; Coleman, P.; James, R, Dioxins in ambient air, bonfire night 1994. Chemosphere 1997, 34, 1191-1201.

Fiedler, H.; Sources of PCDD/PCDF and Impact on the Environment. Chemosphere 1996, . 32, 55-64.

Frederiksen, M.; Meyer, H.W.; Ebbehøy, E.; Gunnarsen, L. Polychlorinated biphenyls (PCBs) in indoor air originating from sealants in contaminated and uncontaminated apartments within the same housing estate. Chemosphere 2012, 89, 473-479.

Harrad, S.; Hazrati, S.; Ibarra C. Concentrations of Polychlorinated Biphenyls in Indoor Air and Polybrominated Diphenyl Ethers in Indoor Air and Dust in Birmingham, United Kingdom: Implications for Human Exposure. Environ. Sci. Technol. 2006, 40, 4633-4638.

Harrad, S.; Goosey, E.; Desborough, J.; Abdallah, M.A.E.; Roosens, L.; Covaci, A. Dust from U.K. Primary School Classrooms and Daycare Centers: The Significance of Dust As a Pathway of Exposure of Young U.K. Children to Brominated Flame Retardants and Polychlorinated Biphenyls. Environ. Sci. Technol. 2010, 44, 4198–4202.

Helsel, D.R. Summing Nondetects: Incorporating Low-Level Contaminants in Risk Assessment. Integr Environ. Assess. Manag. 2010, 6, 361-366.

Hippelein, M.; McLachlan, M. Soil/Air Partitioning of Semivolatile Organic Compounds. 1. Method Development and Influence of Physical-Chemical Properties. Environ. Sci. Technol. 1998, 32, 310-316.

Hippelein, M.; McLachlan, M. Soil/Air Partitioning of Semivolatile Organic Compounds. 2. Influence of Temperature and Relative Humidity. Environ. Sci. Technol. 2000, 34, 3521-3526.

Irvine, K.N.; Loganathan, B.G. Localized enrichment of PCB levels in street dust due to redistribution by wind. Water, Air and Soil Pollution 1998, 105, 603–615.

Kaupp, H.; Towara, J.; McLachlan, M.S. Distribution of polychlorinated dibenzo-p-dioxins and dibenzofurans in atmospheric particulate matter with respect to particle size. Atmos. Environ. 1994, 28, 585–593.

Klees, M.; Hiester, E.; Bruckmann, P.; Schmidt, T.C. Determination of polychlorinated biphenyls and polychlorinated dibenzo-p-dioxins and dibenzofurans by pressurized liquid extraction and gas chromatography coupled to mass spectrometry in street dust samples. J. Chromatogr. A 2013, 1300, 17-23.

Koester, C.J.; Hites, R.A. Wet and dry deposition of chlorinated dioxins and furans. Environ. Sci. Technol. 1992, 26, 1375-1382.

Leung, A.O.W.; Zheng, J.; Yu, C.K.; Liu, W.K.; Wong, C.K.C.; Cai, Z.; Wong, M.H. Polybrominated diphenyl ethers and polychlorinated dibenzop-dioxins and dibenzofurans in surface dust at an e-waste processing site in Southeast China. Environ. Sci. Technol. 2011, 45, 5775–5782.

Li, Z., Feng, X., Li, G., Bi, X., Zhu, J., Qin, H., Dai, Z., Liu, J., Li, Q., Sun, G. Distributions, sources and pollution status of 17 trace metal/metalloids in the street dust of a heavily industrialized city of central China. Environ. Pol. 2013, 182 408-416.

Loganathan, B.G., Irvine, K.N., Kannan, K., Pragatheeswaran, V., Sajwan, K.S. Distribution of Selected PCB Congeners in the Babcock Street Sewer District: A Multimedia Approach to Identify PCB Sources in Combined Sewer Overflows (CSOs) Discharging to the Buffalo River, New York. Arch. Environ. Contam. Toxicol. 1997 33, 130–140.

Lohmann, R.; Lee, R.G.M; Green, N.J.L., Jones, K.C. Gas-particle partitioning of PCDD/Fs in daily air samples. Atmos. Environ. 2000, 34, 2529-2537.

Mandalakis, M.; Tsapakis, M.; Tsoga, A.; Stephanou E.G. Gas–particle concentrations and distribution of aliphatic hydrocarbons, PAHs, PCBs and PCDD/Fs in the atmosphere of Athens (Greece). Atmos. Environ. 2002, 36, 4023–4035.

Martinez, M.; Diaz-Ferrero, J.D.; Marti, R.; Broto-Puig, F.; Comellas, L.; Rodriguez-Larana, M.C. Analysis of dioxin-like compounds in vegetation and soil samples burned in Catalan forest fires. Comparison with the corresponding unburned material. Chemosphere 2000, 41, 1927-1935.

Ogura, I.; Masunaga, S.; Nakanishi, J. Congener-specific characterization of PCDDs/PCDFs in atmospheric deposition: comparison of profiles among deposition, source, and environmental sink. Chemosphere 2001, 45, 173-183.

Okorie A., Entwistle, J., Dean, J.R. Estimation of daily intake of potentially toxic elements from urban street dust and the role of oral bioaccessibility testing. Chemosphere 2012, 86, 460-467.

Petroleum products and used oils. Determination of PCBs and related products. Part 2: Calculation of polychlorinated biphenyl (PCB) content; German version EN 12766-2:2001

Quaß, U.; Fermann, M.; Bröker, G. The European Dioxin Air Emission Inventory Project—Final Results. Chemosphere 2004, 54, 1319-1327.

R. A Language and Environment for Statistical Computing, R Foundation for Statistical Computing, Vienna 2013. www.r-project.org

Regulation 76/2000/EC of the european parliament and board and of the council on the incineration of waste, 04.12.2000, L 332/91.

Regulation 850/2004/EC of the european parliament and board dealing with persistent organic pollutants, 30.04.2004, L 158.

Schuster, J. K.; Gioia, R.; Breivik K.; Steinnes, E.; Scheringer, M.; Jones, K.C. Trends in european background air reflect reductions in primary emissions of PCBs and PBDEs. Environ. Sci. Technol. 2010a, 44, 6760–6766.

Schuster, J.K.; Gioia, R.; Sweetman, A.J.; Jones, K.C. Temporal trends and controlling factors for polychlorinated biphenyls in the UK atmosphere (1991-2008). Environ. Sci. Technol. 2010b, 44, 8068–8074.

Schwerpunktinspektionsprogramm PCB. Inspektion von Anlagen, in denen PCB-haltiger-Abfall anfällt oder entsorgt wird. LANUV-Fachbericht 39. ISSN 1864-3930 LANUV-Fachberichte. 2012.

Siebzehnte Verordnung zur Durchführung des Bundes-Immissionsschutzgesetzes (Verordnung über die Verbrennung und die Mitverbrennung von Abfällen - 17. BImSchV) 17. BImSchV Ausfertigungsdatum: 23.11.1990.

Sinkkonen, S.; Paasivirta, J. Degradation half-life times of PCDDs, PCDFs and PCBs for environmental fate modelling. Chemosphere 2000, 40, 943-949.

Stationary source emissions – determination of the mass concentration of PCDDs/PCDFs and dioxin-like PCBs – Part 2: extraction and clean-up of PCDDs/PCDFs; German version EN 1948-2:2006a.

Stationary source emissions – determination of the mass concentration of PCDDs/PCDFs and dioxin-like PCBs – Part 3: identification and quantification of PCDDs/PCDFs; German version EN 1948-3:2006b.

Stationary source emissions – determination of the mass concentration of PCDDs/PCDFs and dioxin-like PCBs – Part 4: sampling and analysis of dioxin-like PCBs; German version EN 1948-4:2010.

Stockholm Convention on Persistent Organic Pollutants (POPs). Stockholm. 2009. http://chm.pops.int/TheConvention/ConventionText/tabid/2232/Default.aspx

UNEP. Guidance on the Global Monitoring Plan for Persistent Organic Pollutants. UNEP/CHEMICALS/2007/2, 2007.

van den Berg, M.; Birnbaum, L. S.; Denison, M. ; De Vito, M. ; Farland, W. ; Feeley, M.; Fiedler, H.; Hakansson, H.; Hanberg, A.; Haws, L.; Rose, M.; Safe, S.; Schrenk, D.; Tohyama, C.; Tritscher, A.; Tuomisto, J.; Tysklind, M.; Walker, N.; Peterson, R. E. The 2005

World Health Organization Re-evaluation of Human and Mammalian Toxic Equivalency Factors for Dioxins and Dioxin-like Compounds. Toxicol. Sci. 2006, 93, 223-241.

van der Loo, M.P.J. Extremevalues – a package for outlier detection; R package version 2.0 2010a.

van der Loo, M.P.J. Distribution based outlier detection for univariate data. Statistics Netherlands 2010b 10003 The Hague/Heerlen.

Wang, W., Wu, F., Zheng, J., Wong, M.H. Risk assessments of PAHs and Hg exposure via settled house dust and street dust, linking with their correlations in human hair. J. Hazard Mater. 2013, 263, 627– 637.

Wittsiepe, J.; Ewers, U.; Mergner, H.J.; Lahm, B.; Hansen, D.; Volland, G.; Schrey, P. PCDD/F-content in house dust. Zentralbl. Hyg. Umweltmed. 1997, 6, 537-50.

Wong F.; Bidleman, T. Aging of Organochlorine Pesticides and Polychlorinated Biphenyls in Muck Soil: Volatilization, Bioaccessibility and Degradation. Environ. Sci. Technol. 2011, 45, 958-963.

Yang, Y.; Baumann, W. Study of polychlorinated biphenyls in street dust by supercritical fluid extraction gas chromatography/mass spectrometry. Fresenius J. Anal. Chem. 1996, 354, 56-60.

Zakaria, M.P., Takada, H., Tsutsumi, S., Ohno, K., Yamada, J., Kouno, E., Kumata, H. Distribution of Polycyclic Aromatic Hydrocarbons (PAHs) in Rivers and Estuaries in Malaysia: A Widespread Input of Petrogenic PAHs. Environ. Sci. Technol. 2002, 36, 1907–1918.

3.6 Supporting Information

Table S 10 Blank values for individual PCB and PCDD/PCDF congeners and homologues are shown. In addition blank standard deviations were depicted and the calculated limit of detection of the method (LOD) is shown.

	blank value (PCBs n=7; PCDD/PCDF n=4)	LOD (the limit of detection)
PCB homologues	**(ng/Sample)**	**(ng/Sample)**
TriPCBs	2.5 ± 1.9	8.2
TetraPCBs	5.8 ± 3.3	16
PentaPCBs	10 ± 5.6	27
HexaPCBs	14 ± 7.4	36
HeptaPCBs	4.6 ± 2.5	12
OctaPCBs	0.95 ± 0.62[b]	2.8
NonaPCBs	0.043[c]	0.043
DecaPCB	< 0.029	0.11
PCB congeners	**(ng/Sample)**	**(ng/Sample)**
PCB #28	0.37 ± 0.27	1.2
PCB #52	0.66 ± 0.30	1.6
PCB #101	2.4 ± 1.6	7.1
PCB #153	2.6 ± 1.6	7.3
PCB #138	2.9 ± 1.7	7.9
PCB #180	1.4 ± 0.97	4.3
PCB #81	0.014 ± 0.0070	0.036
PCB #77	0.054 ± 0.036	0.16
PCB #126	0.0043 ± 0.0027	0.012
PCB #169	0.0013 ± 0.00096	0.0041
PCB #123	0.12 ± 0.036	0.23
PCB #118	0.86 ± 0.52	2.4
PCB #114	0.018 ± 0.0019	0.075
PCB #105	0.22 ± 0.14	0.65
PCB #167	0.13 ± 0.072	0.35
PCB #156	0.26 ± 0.15	0.69
PCB #157	0.053 ± 0.0552	0.22
PCB #189	0.031 ± 0.026	0.11
TEQ excl. LOD	0.00071 ± 0.00043	-
TEQ ½ LOD	0.00074 ± 0.00042	0.00076
TEQ incl. LOD	0.00076 ± 0.00040	-
PCDD/PCDF homologues	**(pg/Sample)**	**(pg/Sample)**
TCDD	0.45 ± 0.62	2.3
PCDD	0.65 ± 0.87	3.3
HxCDD	1.8 ± 2.4	9.1
HpCDD	4.0 ± 6.3	23
OCDD	11 ± 18	63
TCDF	5.3 ± 6.9	26
PCDF	2.3 ± 3.7	13
HxCDF	2.3 ± 2.6	10
HpCDF	1.8 ± 2.1	8.1
OCDF	3.7 ± 4.4	17
PCDD/PCDF congeners	**(pg/Sample)**	**(pg/Sample)**
2,3,7,8-TCDD	-	-
1,2,3,7,8-PeCDD	-	-
1,2,3,4,7,8-HxCDD	-	-
1,2,3,6,7,8-HxCDD	-	-
1,2,3,7,8,9-HxCDD	-	-
1,2,3,4,6,7,8-HpCDD	2.0 ± 3.1	11
2,3,7,8-TCDF	-	-
1,2,3,7,8-PeCDF	-	-
2,3,4,7,8-PeCDF	-	-
1,2,3,4,7,8-HxCDF	-	-
1,2,3,6,7,8-HxCDF	-	-
1,2,3,7,8,9-HxCDF	-	-
2,3,4,6,7,8-HxCDF	-	-
1,2,3,4,6,7,8-HpCDF	0.94 ± 1.1	4.3
1,2,3,4,7,8,9-HpCDF		
TEQ excl. LOD	-	-
TEQ ½ LOD	-	-
TEQ incl. LOD	-	-

Table S 11 Congener and homologue specific concentrations of PCBs and PCDD/PCDFs in UI1

UI1	<2000 µm >1000µm	<1000 µm >500 µm	<500 µm >250µm	<250 µm >125µm	<125 µm >63 µm	< 63 µm
PCB homologues	**(µg//kg)**	**(µg//kg)**	**(µg//kg)**	**(µg//kg)**	**(µg//kg)**	**(µg//kg)**
TriPCBs	< 8.2	< 8.2	< 8.2	9.3	10	15
TetraPCBs	< 16	< 16	< 16	< 16	21	40
PentaPCBs	< 27	< 27	< 27	< 27	39	47
HexaPCBs	< 36	< 36	< 36	< 36	71	53
HeptaPCBs	< 12	< 12	< 12	< 12	36	22
OctaPCBs	< 2.8	< 2.8	< 2.8	< 2.8	8.1	3.2
NonaPCBs	< 0.043	< 0.043	< 0.043	< 0.043	0.21	0.37
DecaPCB	< 0.11	< 0.11	< 0.11	< 0.11	0.112	0.11
PCB congeners	**(µg//kg)**	**(µg//kg)**	**(µg//kg)**	**(µg//kg)**	**(µg//kg)**	**(µg//kg)**
PCB #28	< 1.2	< 1.2	< 1.2	< 1.2	1.2	2.0
PCB #52	< 1.6	< 1.6	< 1.6	< 1.6	2.2	2.9
PCB #101	< 7.1	< 7.1	< 7.1	< 7.1	7.5	< 7.1
PCB #153	< 7.3	< 7.3	< 7.3	< 7.3	13	9.2
PCB #138	< 7.9	< 7.9	< 7.9	< 7.9	17	13
PCB #180	< 4.3	< 4.3	< 4.3	< 4.3	9.8	5.6
PCB #81	< 0.036	< 0.036	0.046	0.042	0.081	0.11
PCB #77	< 0.16	< 0.16	< 0.16	< 0.16	0.27	0.46
PCB #126	< 0.012	< 0.012	< 0.012	0.023	0.063	0.082
PCB #169	< 0.0041	< 0.0041	< 0.0041	< 0.0041	0.0079	0.011
PCB #123	< 0.23	< 0.23	< 0.23	< 0.23	0.64	0.63
PCB #118	< 2.4	< 2.4	< 2.4	< 2.4	3.2	5.4
PCB #114	< 0.075	< 0.075	< 0.075	< 0.075	0.16	0.13
PCB #105	< 0.65	< 0.65	< 0.65	< 0.65	1.0	2.3
PCB #167	< 0.35	< 0.35	< 0.35	< 0.35	0.71	0.61
PCB #156	< 0.69	< 0.69	< 0.69	< 0.69	1.3	1.0
PCB #157	< 0.22	< 0.22	< 0.22	< 0.22	0.26	0.26
PCB #189	< 0.11	< 0.11	< 0.11	< 0.11	0.29	0.15
TEQ excl. LOD	-	-	0.00001	0.0024	0.0068	0.0089
TEQ ½ LOD	0.00076	0.00076	0.00090	0.0025	0.0068	0.0089
TEQ incl. LOD	-	-	0.0018	0.0026	0.0068	0.0089
PCDD/PCDF homologues	**(ng/kg)**	**(ng/kg)**	**(ng/kg)**	**(ng/kg)**	**(ng/kg)**	**(ng/kg)**
TCDD	< 2.3	< 2.3	2.7	6.2	9.8	17
PCDD	< 3.3	< 3.3	< 3.3	6.4	22	21
HxCDD	< 9.1	< 9.1	< 9.1	12	51	55
HpCDD	< 23	< 23	< 23	< 23	65	83
OCDD	< 63	< 63	< 63	< 63	153	176
TCDF	< 26	26	< 26	43	102	158
PCDF	< 13	13	< 13	33	105	121
HxCDF	< 10	10	11	33	120	135
HpCDF	< 8.1	8.1	< 8.1	13	53	71
OCDF	< 17	17	< 17	< 17	26	39
PCDD/PCDF congeners	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)
2,3,7,8-TCDD	< 0.30	< 0.19	< 0.27	0.74	0.32	0.61
1,2,3,7,8-PeCDD	< 0.41-	0.056	< 0.17	0.48	0.54	0.79
1,2,3,4,7,8-HxCDD	0.11	< 0.068	< 0.31	< 0.87	0.62	1.3
1,2,3,6,7,8-HxCDD	0.49	0.13	0.48	< 0.76	2.1	3.8
1,2,3,7,8,9-HxCDD	0.23	< 0.14	< 0.32	< 1.1	1.5	2.4
1,2,3,4,6,7,8-HpCDD	< 12	< 12	< 12	< 12	33	39
2,3,7,8-TCDF	0.34	0.69	0.92	1.8	3.3	6.8
1,2,3,7,8-PeCDF	0.32	0.50	0.83	2.6	8.0	9.6
2,3,4,7,8-PeCDF	0.42	0.33	0.53	1.8	6.6	8.5
1,2,3,4,7,8-HxCDF	0.29	0.41	0.93	1.9	8.6	11
1,2,3,6,7,8-HxCDF	< 0.18	0.37	0.77	2.9	15	15
1,2,3,7,8,9-HxCDF	< 0.14	< 0.056	0.34	0.97	3.8	4.3
2,3,4,6,7,8-HxCDF	2.9	3.0	3.5	6.1	16	19
1,2,3,4,6,7,8-HpCDF	< 4.3	< 4.3	4.3	8.7	36	48
1,2,3,4,7,8,9-HpCDF	< 0.53	< 0.086	0.56	1.5	7.9	12
TEQ excl. LOD	0.57	0.63	0.88	3.3	9.0	12
TEQ ½ LOD	1.0	0.83	1.2	3.5	9.0	12
TEQ incl. LOD	1.5	1.0	1.6	3.7	9.0	12

Table S 12 Congener and homologue specific concentrations of PCBs and PCDD/PCDFs in UI2

UI2	<2000 µm >1000µm	<1000 µm >500 µm	<500 µm >250µm	<250 µm >125µm	<125 µm >63 µm	< 63 µm
PCB homologues	**(µg//kg)**	**(µg//kg)**	**(µg//kg)**	**(µg//kg)**	**(µg//kg)**	**(µg//kg)**
TriPCBs	13	18	24	34	40	95
TetraPCBs	35	33	51	90	109	238
PentaPCBs	42	47	75	112	131	325
HexaPCBs	58	48	84	120	108	250
HeptaPCBs	22	19	32	45	41	81
OctaPCBs	< 2.8	< 2.8	3.8	4.4	5.2	9.0
NonaPCBs	0.11	< 0.043	0.36	0.23	0.22	0.27
DecaPCB	< 0.11	< 0.11	< 0.11	< 0.11	0.22	0.15
PCB congeners	**(µg//kg)**	**(µg//kg)**	**(µg//kg)**	**(µg//kg)**	**(µg//kg)**	**(µg//kg)**
PCB #28	1.6	2.0	2.7	4.6	8.6	18
PCB #52	2.1	3.0	4.3	6.2	8.3	20
PCB #101	< 7.1	8.1	13	20	20	51
PCB #153	11	8.0	14	21	17	38
PCB #138	15	11	20	29	26	59
PCB #180	6.4	4.7	8.6	12	11	21
PCB #81	0.10	0.14	0.20	0.30	0.40	0.98
PCB #77	0.32	0.40	0.65	1.0	1.6	4.1
PCB #126	0.067	0.045	0.088	0.13	0.16	0.31
PCB #169	0.010	0.012	0.016	0.030	0.030	0.040
PCB #123	0.43	0.35	0.62	0.83	0.93	2.6
PCB #118	4.7	5.6	8.6	14	18	44
PCB #114	0.088	0.078	0.14	0.23	0.46	1.1
PCB #105	1.9	2.4	3.7	4.7	7.8	21
PCB #167	0.74	0.54	0.92	1.5	1.6	3.7
PCB #156	1.2	1.0	1.7	3.0	3.2	7.4
PCB #157	0.29	0.28	0.44	0.62	0.85	2.1
PCB #189	0.15	0.14	0.24	0.35	0.33	0.64
TEQ excl. LOD	0.0074	0.0052	0.0099	0.015	0.018	0.036
TEQ ½ LOD	0.0074	0.0052	0.0099	0.015	0.018	0.036
TEQ incl. LOD	0.0074	0.0052	0.0099	0.015	0.018	0.036
PCDD/PCDF homologues	**(ng/kg)**	**(ng/kg)**	**(ng/kg)**	**(ng/kg)**	**(ng/kg)**	**(ng/kg)**
TCDD	38	34	40	68	57	104
PCDD	90	70	88	168	136	190
HxCDD	156	109	158	310	252	357
HpCDD	68	62	97	246	243	294
OCDD	< 63	< 63	66	178	168	260
TCDF	254	231	276	538	793	1027
PCDF	255	290	306	678	734	857
HxCDF	242	205	276	728	776	924
HpCDF	101	76	111	290	314	305
OCDF	41	35	45	90	88	< 17
PCDD/PCDF congeners	**(ng/kg)**	**(ng/kg)**	**(ng/kg)**	**(ng/kg)**	**(ng/kg)**	**(ng/kg)**
2,3,7,8-TCDD	1.2	0.58	0.72	0.70	0.72	2.3
1,2,3,7,8-PeCDD	3.4	3.3	3.3	6.0	5.6	4.6
1,2,3,4,7,8-HxCDD	3.4	3.0	3.1	6.7	4.4	5.8
1,2,3,6,7,8-HxCDD	6.8	5.6	8.0	18	17	20
1,2,3,7,8,9-HxCDD	7.4	4.8	6.4	13	11	10
1,2,3,4,6,7,8-HpCDD	33	30	47	124	111	144
2,3,7,8-TCDF	10	8.4	9.2	17	17	31
1,2,3,7,8-PeCDF	20	22	23	54	65	66
2,3,4,7,8-PeCDF	18	17	18	42	38	60
1,2,3,4,7,8-HxCDF	24	19	23	53	54	67
1,2,3,6,7,8-HxCDF	23	20	31	85	77	92
1,2,3,7,8,9-HxCDF	1.6	3.0	6.8	20	27	15
2,3,4,6,7,8-HxCDF	24	19	30	86	87	107
1,2,3,4,6,7,8-HpCDF	59	51	77	192	216	245
1,2,3,4,7,8,9-HpCDF	12	6.0	3.1	42	42	18
TEQ excl. LOD	22	19	23	54	53	66
TEQ ½ LOD	22	19	23	54	53	66
TEQ incl. LOD	22	19	23	54	53	66

Table S 13 Congener and homologue specific concentrations of PCBs and PCDD/PCDFs in UI3

UI3	<2000 µm >1000µm	<1000 µm >500 µm	<500 µm >250µm	<250 µm >125µm	<125 µm >63 µm	< 63 µm
PCB homologues	**(µg//kg)**	**(µg//kg)**	**(µg//kg)**	**(µg//kg)**	**(µg//kg)**	**(µg//kg)**
TriPCBs	15	19	15	29	40	72
TetraPCBs	19	34	29	52	85	165
PentaPCBs	< 27	48	46	63	117	217
HexaPCBs	< 36	42	< 36	46	89	166
HeptaPCBs	< 12	< 12	< 12	15	30	53
OctaPCBs	< 2.8	< 2.8	< 2.8	< 2.8	3.3	6.5
NonaPCBs	< 0.043	< 0.043	< 0.043	0.072	0.11	0.30
DecaPCB	< 0.11	< 0.11	< 0.11	< 0.11	0.11	0.12
PCB congeners	(µg//kg)	(µg//kg)	(µg//kg)	(µg//kg)	(µg//kg)	(µg//kg)
PCB #28	1.7	2.5	2.7	4.3	7.1	13
PCB #52	1.6	3.3	4.3	4.6	7.4	14
PCB #101	< 7.1	8.1	13	9.6	20	33
PCB #153	< 7.3	< 7.3	14	< 7.3	14	25
PCB #138	< 7.9	9.2	20	11	21	38
PCB #180	< 4.3	< 4.3	8.6	< 4.3	8.0	14
PCB #81	0.058	0.14	0.12	0.18	0.34	0.66
PCB #77	0.22	0.49	0.44	0.67	1.1	2.4
PCB #126	0.014	0.039	0.030	0.057	0.12	0.22
PCB #169	0.0044	0.0077	0.0053	0.0098	0.019	0.025
PCB #123	< 0.23	0.31	0.31	0.48	0.80	1.8
PCB #118	2.6	5.3	5.5	7.2	13	26
PCB #114	< 0.075	2.3	0.13	0.16	0.27	0.75
PCB #105	1.2	0.64	2.6	3.2	5.6	13
PCB #167	< 0.35	0.47	0.43	0.60	1.1	2.3
PCB #156	< 0.69	0.86	0.75	1.1	2.0	4.5
PCB #157	< 0.22	< 0.22	< 0.22	0.31	0.58	1.3
PCB #189	< 0.11	< 0.11	< 0.11	< 0.11	0.11	0.18
TEQ excl. LOD	0.0017	0.0045	0.0036	0.0065	0.014	0.025
TEQ ½ LOD	0.0017	0.0045	0.0036	0.0065	0.014	0.025
TEQ incl. LOD	0.0017	0.0045	0.0036	0.0065	0.014	0.025
PCDD/PCDF homologues	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)
TCDD	< 2.3	< 2.3	< 2.3	5.1	12	20
PCDD	< 3.3	< 3.3	5.5	12	31	29
HxCDD	< 9.1	< 9.1	< 9.1	34	65	98
HpCDD	< 23	< 23	< 23	48	90	152
OCDD	< 63	< 63	< 63	200	105	186
TCDF	< 26	< 26	39	89	230	430
PCDF	< 13	16	25	95	241	394
HxCDF	15	14	21	97	275	398
HpCDF	< 8.1	< 8.1	8.5	51	123	184
OCDF	51	< 17	< 17	29	47	83
PCDD/PCDF congeners	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)
2,3,7,8-TCDD	< 0.65	< 0.46	< 0.24	< 0.82	0.68	0.97
1,2,3,7,8-PeCDD	< 1.1	< 0.97	0.46	0.59	1.6	1.5
1,2,3,4,7,8-HxCDD	< 1.4	< 0.17	< 0.23	0.98	1.4	2.5
1,2,3,6,7,8-HxCDD	< 2.0	0.17	< 0.15	2.9	5.5	8.2
1,2,3,7,8,9-HxCDD	< 0.62	< 0.11	< 0.21	1.8	3.0	4.4
1,2,3,4,6,7,8-HpCDD	< 12	< 12	< 12	27	45	75
2,3,7,8-TCDF	< 0.72	0.88	0.94	2.6	4.8	7.5
1,2,3,7,8-PeCDF	< 0.94	1.2	2.6	7.7	19	27
2,3,4,7,8-PeCDF	< 1.5	1.0	1.4	5.6	15	21
1,2,3,4,7,8-HxCDF	1.6	0.81	1.9	7.6	20	29
1,2,3,6,7,8-HxCDF	1.5	1.1	2.1	12	37	56
1,2,3,7,8,9-HxCDF	< 1.3	< 0.24	0.37	3.1	8.5	16
2,3,4,6,7,8-HxCDF	5.0	5.0	5.6	16	40	59
1,2,3,4,6,7,8-HpCDF	<4.3	4.6	7.2	32	80	118
1,2,3,4,7,8,9-HpCDF	< 1.4	< 0.12	0.75	7.9	21	36
TEQ excl. LOD	0.87	1.2	2.1	8.0	21	30
TEQ ½ LOD	2.4	2.0	2.3	8.4	21	30
TEQ incl. LOD	3.9	2.8	2.6	8.8	21	30

Table S 14 Congener and homologue specific concentrations of PCBs and PCDD/PCDFs in UI4

UI4	<2000 µm >1000µm	<1000 µm >500 µm	<500 µm >250µm	<250 µm >125µm	<125 µm >63 µm	< 63 µm
PCB homologues	**(µg//kg)**	**(µg//kg)**	**(µg//kg)**	**(µg//kg)**	**(µg//kg)**	**(µg//kg)**
TriPCBs	10	28	14	9.3	19	35
TetraPCBs	20	41	28	34	54	78
PentaPCBs	27	30	27	57	43	83
HexaPCBs	36	36	36	102	62	115
HeptaPCBs	< 12	< 12	< 12	46	32	52
OctaPCBs	< 2.8	< 2.8	< 2.8	5.2	6.5	8.6
NonaPCBs	< 0.043	< 0.043	< 0.043	0.35	0.52	0.97
DecaPCB	< 0.11	< 0.11	< 0.11	< 0.11	0.15	0.17
PCB congeners	(µg//kg)	(µg//kg)	(µg//kg)	(µg//kg)	(µg//kg)	(µg//kg)
PCB #28	1.5	4.4	1.7	1.5	3.4	5.1
PCB #52	1.6	3.5	1.8	3.5	3.8	6.1
PCB #101	< 7.1	< 7.1	< 7.1	11	7.8	14
PCB #153	< 7.3	< 7.3	< 7.3	19	10	20
PCB #138	< 7.9	< 7.9	< 7.9	22	12	25
PCB #180	< 4.3	< 4.3	< 4.3	13	8.2	14
PCB #81	0.046	0.094	0.048	0.16	0.35	0.71
PCB #77	0.20	0.45	0.24	0.49	5.1	10
PCB #126	0.016	0.025	0.014	0.072	0.15	0.28
PCB #169	0.0053	0.0045	0.0041	0.0079	2.6	4.9
PCB #123	< 0.23	< 0.23	< 0.23	0.50	1.3	2.2
PCB #118	< 2.4	3.2	< 2.4	5.9	0.28	0.41
PCB #114	< 0.075	< 0.075	< 0.075	0.13	0.37	0.38
PCB #105	< 0.64	1.4	< 0.64	2.2	0.35	0.71
PCB #167	< 0.35	< 0.35	< 0.35	0.92	5.1	10
PCB #156	< 0.69	< 0.69	< 0.69	1.7	0.15	0.28
PCB #157	< 0.22	< 0.22	< 0.22	0.23	2.6	4.9
PCB #189	< 0.11	< 0.11	< 0.11	0.29	0.46	1.2
TEQ excl. LOD	**0.0018**	**0.0028**	**0.0016**	**0.0079**	**0.0084**	**0.015**
TEQ ½ LOD	**0.0018**	**0.0029**	**0.0017**	**0.0079**	**0.0084**	**0.015**
TEQ incl. LOD	**0.0019**	**0.0029**	**0.0017**	**0.0079**	**0.0084**	**0.015**
PCDD/PCDF homologues	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)
TCDD	3.0	4.2	< 2.3	5.8	8.2	17
PCDD	< 3.3	9.8	4.7	7.3	24	31
HxCDD	19	14	15	19	36	74
HpCDD	68	< 23	< 23	< 23	48	115
OCDD	212	< 63	< 63	< 63	159	414
TCDF	< 26	< 26	26	36	61	108
PCDF	14	< 13	13	25	36	74
HxCDF	16	< 10	13	30	50	71
HpCDF	< 8.1	< 8.1	8.1	12	24	50
OCDF	< 17	< 17	< 17	18	< 17	< 17
PCDD/PCDF congeners	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)
2,3,7,8-TCDD	< 0.084	0.83	0.77	1.0	1.0	1.2
1,2,3,7,8-PeCDD	< 0.066	< 0.10	0.15	0.16	0.29	1.0
1,2,3,4,7,8-HxCDD	0.94	0.22	0.19	0.20	0.42	1.7
1,2,3,6,7,8-HxCDD	0.99	0.75	0.52	0.96	1.1	3.2
1,2,3,7,8,9-HxCDD	0.43	< 0.11	0.21	0.52	1.1	2.8
1,2,3,4,6,7,8-HpCDD	41	< 12	< 12	< 12	25	58
2,3,7,8-TCDF	0.76	0.80	0.98	1.8	2.8	5.2
1,2,3,7,8-PeCDF	0.96	0.80	0.74	1.6	2.8	6.2
2,3,4,7,8-PeCDF	1.1	0.52	0.59	1.5	1.9	4.8
1,2,3,4,7,8-HxCDF	1.5	0.83	1.1	1.8	3.6	8.9
1,2,3,6,7,8-HxCDF	0.54	0.39	0.52	1.4	2.4	5.2
1,2,3,7,8,9-HxCDF	< 0.034	< 0.090	0.14	0.32	0.80	0.96
2,3,4,6,7,8-HxCDF	3.6	4.3	4.2	5.7	6.8	8.7
1,2,3,4,6,7,8-HpCDF	< 4.3	< 4.3	< 4.3	8.6	17	37
1,2,3,4,7,8,9-HpCDF	< 0.018	< 0.31	0.43	0.46	0.64	2.0
TEQ excl. LOD	**1.7**	**1.7**	**1.9**	**3.0**	**4.3**	**8.6**
TEQ ½ LOD	**1.8**	**1.9**	**2.0**	**3.1**	**4.3**	**8.6**
TEQ incl. LOD	**1.9**	**2.1**	**2.1**	**3.2**	**4.4**	**8.6**

Table S 15 Congener and homologue specific concentrations of PCBs and PCDD/PCDFs in UI5

UI5	<2000 µm >1000µm	<1000 µm >500 µm	<500 µm >250µm	<250 µm >125µm	<125 µm >63 µm	< 63 µm
PCB homologues	**(µg//kg)**	**(µg//kg)**	**(µg//kg)**	**(µg//kg)**	**(µg//kg)**	**(µg//kg)**
TriPCBs	< 8.2	< 8.2	9.3	11	19	< 8.2
TetraPCBs	18	< 16	19	32	106	145
PentaPCBs	< 27	< 27	< 27	37	60	164
HexaPCBs	< 36	< 36	< 36	36	43	125
HeptaPCBs	< 12	< 12	< 12	12	15	43
OctaPCBs	< 2.8	< 2.8	< 2.8	< 2.8	2.8	5.8
NonaPCBs	0.082	< 0.043	< 0.043	< 0.043	0.078	< 0.043
DecaPCB	< 0.11	< 0.11	< 0.11	< 0.11	< 0.11	< 0.11
PCB congeners	(µg//kg)	(µg//kg)	(µg//kg)	(µg//kg)	(µg//kg)	(µg//kg)
PCB #28	< 1.2	< 1.2	1.3	2.2	3.5	12
PCB #52	< 1.6	< 1.6	< 1.6	2.5	4.0	9.5
PCB #101	< 7.1	< 7.1	< 7.1	< 7.1	< 7.1	24
PCB #153	< 7.3	< 7.3	< 7.3	< 7.3	< 7.3	20
PCB #138	< 7.9	< 7.9	< 7.9	< 7.9	10	30
PCB #180	< 4.3	< 4.3	< 4.3	< 4.3	< 4.3	12
PCB #81	0.052	0.052	0.061	0.097	0.16	0.42
PCB #77	0.19	< 0.16	0.21	0.37	0.67	1.8
PCB #126	0.023	0.017	0.021	0.034	0.057	0.14
PCB #169	< 0.041	< 0.041	0.0046	0.0051	0.0063	0.014
PCB #123	< 0.23	< 0.23	< 0.23	0.50	0.41	0.94
PCB #118	< 2.4	< 2.4	< 2.4	5.9	6.2	19
PCB #114	< 0.075	< 0.075	< 0.075	0.13	0.18	0.49
PCB #105	0.87	0.71	0.96	2.2	3.2	8.5
PCB #167	< 0.35	< 0.35	< 0.35	< 0.35	0.50	1.6
PCB #156	< 0.69	< 0.69	< 0.69	< 0.69	1.0	3.1
PCB #157	0.24	0.24	0.24	0.24	0.28	0.86
PCB #189	< 0.11	< 0.11	< 0.11	< 0.11	0.11	0.14
TEQ excl. LOD	**0.0024**	**0.0018**	**0.0023**	**0.0038**	**0.0063**	**0.016**
TEQ ½ LOD	**0.0025**	**0.0019**	**0.0023**	**0.0038**	**0.0063**	**0.016**
TEQ incl. LOD	**0.0026**	**0.0020**	**0.0024**	**0.0038**	**0.0063**	**0.016**
PCDD/PCDF homologues	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)
TCDD	4.8	< 2.3	< 2.3	< 2.3	4.6	14
PCDD	< 3.3	< 3.3	< 3.3	< 3.3	5.6	12
HxCDD	< 9.1	< 9.1	< 9.1	< 9.1	9.5	22
HpCDD	< 23	< 23	< 23	< 23	23	34
OCDD	< 63	< 63	< 63	< 63	64	70
TCDF	< 26	< 26	< 26	< 26	29	69
PCDF	< 13	< 13	< 13	< 13	18	85
HxCDF	< 10	< 10	< 10	< 10	20	32
HpCDF	< 8.1	< 8.1	< 8.1	< 8.1	< 8.1	13
OCDF	< 17	< 17	< 17	< 17	< 17	< 17
PCDD/PCDF congeners	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)
2,3,7,8-TCDD	< 0.75	0.41	0.38	0.58	0.36	0.72
1,2,3,7,8-PeCDD	1.7	0.60	0.47	0.40	0.52	0.60
1,2,3,4,7,8-HxCDD	0.64	0.51	0.15	0.46	0.31	0.56
1,2,3,6,7,8-HxCDD	0.65	0.45	0.14	0.49	0.62	1.3
1,2,3,7,8,9-HxCDD	0.69	0.37	0.14	0.47	0.42	0.78
1,2,3,4,6,7,8-HpCDD	< 12	< 12	< 12	< 12	< 12	15
1,2,3,7,8-PeCDF	< 0.60	0.41	0.72	0.60	1.3	5.7
2,3,4,7,8-PeCDF	< 0.35	< 0.22	0.41	0.76	1.1	2.5
1,2,3,4,7,8-HxCDF	< 0.52	0.43	0.48	0.51	1.0	2.8
1,2,3,6,7,8-HxCDF	< 0.48	0.47	0.21	0.57	0.90	2.1
1,2,3,7,8,9-HxCDF	< 0.72	< 0.58	< 0.23	< 0.47	< 0.31	0.22
2,3,4,6,7,8-HxCDF	3.9	2.7	2.7	3.2	3.6	5.7
1,2,3,4,6,7,8-HpCDF	< 4.3	< 4.3	< 4.3	< 4.3	< 4.3	11
1,2,3,4,7,8,9-HpCDF	< 1.1	< 0.69	< 0.12	< 0.29	< 0.8	< 1.1
TEQ excl. LOD	**2.9**	**1.8**	**1.6**	**2.0**	**2.3**	**4.3**
TEQ ½ LOD	**3.6**	**1.9**	**1.7**	**2.1**	**2.4**	**4.3**
TEQ incl. LOD						

Table S 16 Congener and homologue specific concentrations of PCBs and PCDD/PCDFs in U1

U1	<2000 µm >1000µm	<1000 µm >500 µm	<500 µm >250µm	<250 µm >125µm	<125 µm >63 µm	< 63 µm
PCB homologues	**(µg//kg)**	**(µg//kg)**	**(µg//kg)**	**(µg//kg)**	**(µg//kg)**	**(µg//kg)**
TriPCBs		20	23	12	10	19
TetraPCBs		28	31	27	34	33
PentaPCBs		52	78	60	101	105
HexaPCBs		90	170	130	211	227
HeptaPCBs		41	81	75	121	136
OctaPCBs		7.0	10	11	17	19
NonaPCBs		0.55	< 0.043	< 0.043	0.47	0.70
DecaPCB		0.18	< 0.11	< 0.11	0.22	0.26
PCB congeners	(µg//kg)	(µg//kg)	(µg//kg)	(µg//kg)	(µg//kg)	(µg//kg)
PCB #28		< 1.2	1.6	1.4	1.7	1.8
PCB #52		2.1	2.5	2.6	3.8	3.9
PCB #101		11	17	13	21	22
PCB #153		17	30	23	39	42
PCB #138		21	38	29	50	53
PCB #180		10	22	20	32	36
PCB #81		0.11	0.14	0.12	0.19	0.20
PCB #77		0.30	0.34	0.39	0.58	0.62
PCB #126		0.061	0.096	0.11	0.19	0.21
PCB #169		0.012	0.011	0.014	0.021	0.020
PCB #123		0.44	0.91	0.70	1.5	1.4
PCB #118		4.9	6.7	5.2	8.6	8.8
PCB #114		< 0.075	< 0.075	0.077	0.28	< 0.075
PCB #105		1.2	1.6	1.7	2.7	2.7
PCB #167		0.86	1.4	1.2	2.0	2.2
PCB #156		1.7	3.1	2.3	4.0	4.2
PCB #157		0.27	0.32	0.47	0.82	0.65
PCB #189		0.26	0.57	0.51	0.76	0.87
TEQ excl. LOD		**0.0068**	**0.010**	**0.012**	**0.020**	**0.022**
TEQ ½ LOD		**0.0068**	**0.010**	**0.012**	**0.020**	**0.022**
TEQ incl. LOD		**0.0068**	**0.010**	**0.012**	**0.020**	**0.022**
PCDD/PCDF homologues	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)
TCDD		< 2.3	9.8	8.5	20	9.2
PCDD		< 3.3	14	9.8	24	19
HxCDD		47	15	29	50	58
HpCDD		25	< 23	41	58	85
OCDD		< 63	< 63	90	138	231
TCDF		< 26	62	57	104	113
PCDF		26	26	44	83	87
HxCDF		64	24	41	76	86
HpCDF		8.6	13	32	43	63
OCDF		43	31	27	59	76
PCDD/PCDF congeners	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)
2,3,7,8-TCDD		< 0.40	0.98	< 0.95	1.1	1.2
1,2,3,7,8-PeCDD		< 1.2	< 0.18	< 0.67	< 0.56	1.3
1,2,3,4,7,8-HxCDD		< 0.19	< 0.87	0.58	< 0.90	1.7
1,2,3,6,7,8-HxCDD		1.6	< 0.87	1.4	2.1	2.5
1,2,3,7,8,9-HxCDD		2.5	< 0.83	2.3	3.2	4.4
1,2,3,4,6,7,8-HpCDD		< 12	< 12	20	28	43
2,3,7,8-TCDF		< 1.6	3.0	3.9	5.7	7.4
1,2,3,7,8-PeCDF		< 0.40	2.5	2.8	5.9	9.0
2,3,4,7,8-PeCDF		2.6	1.9	3.0	5.2	7.4
1,2,3,4,7,8-HxCDF		3.3	2.9	4.5	7.9	15
1,2,3,6,7,8-HxCDF		< 1.0	0.96	3.1	5.6	8.9
1,2,3,7,8,9-HxCDF		< 0.36	0.55	1.2	1.3	1.8
2,3,4,6,7,8-HxCDF		9.7	6.2	6.4	8.1	10
1,2,3,4,6,7,8-HpCDF		8.1	10	19	29	42
1,2,3,4,7,8,9-HpCDF		0.55	< 0.20	4.4	3.8	6.8
TEQ excl. LOD		**2.6**	**3.1**	**3.8**	**6.9**	**11**
TEQ ½ LOD		**3.6**	**3.4**	**4.6**	**7.2**	**11**
TEQ incl. LOD		**4.6**	**3.7**	**5.4**	**7.6**	**11**

Table S 17 Congener and homologue specific concentrations of PCBs and PCDD/PCDFs in U2

U2	<2000 µm >1000µm	<1000 µm >500 µm	<500 µm >250µm	<250 µm >125µm	<125 µm >63 µm	< 63 µm
PCB homologues	**(µg//kg)**	**(µg//kg)**	**(µg//kg)**	**(µg//kg)**	**(µg//kg)**	**(µg//kg)**
TriPCBs	30	9.5	9.9	< 8.2	22	12
TetraPCBs	< 16	< 16	< 16	17	23	27
PentaPCBs	< 27	< 27	42	45	73	102
HexaPCBs	< 36	< 36	84	91	126	159
HeptaPCBs	< 12	16	34	51	71	84
OctaPCBs	< 2.8	< 2.8	4.7	6.8	8.5	12
NonaPCBs	< 0.043	< 0.043	0.14	0.38	< 0.043	0.48
DecaPCB	0.14	< 0.11	< 0.11	< 0.11	< 0.11	< 0.11
PCB congeners	(µg//kg)	(µg//kg)	(µg//kg)	(µg//kg)	(µg//kg)	(µg//kg)
PCB #28	7.4	< 1.2	< 1.2	< 1.2	2.5	1.3
PCB #52	< 1.6	< 1.6	< 1.6	2.0	3.2	3.4
PCB #101	< 7.1	< 7.1	7.2	9.8	14	17
PCB #153	< 7.3	< 7.3	14	16	24	30
PCB #138	< 7.9	8.3	22	21	31	38
PCB #180	< 4.3	4.3	9.4	13	20	23
PCB #81	0.038	0.046	0.094	0.091	0.19	0.20
PCB #77	< 0.16	< 0.16	0.24	0.27	0.63	0.62
PCB #126	0.014	0.029	0.029	0.055	0.16	0.21
PCB #169	0.0067	0.0043	< 0.0041	0.0064	0.015	0.020
PCB #123	< 0.23	0.29	0.38	0.63	1.0	1.2
PCB #118	< 2.4	< 2.4	6.0	3.7	7.4	8.3
PCB #114	0.095	< 0.075	0.082	< 0.075	< 0.075	0.078
PCB #105	0.87	0.87	2.3	1.4	2.4	2.7
PCB #167	< 0.35	< 0.35	0.97	0.83	1.3	1.5
PCB #156	< 0.69	0.70	2.1	1.6	2.6	3.2
PCB #157	< 0.22	< 0.22	0.36	0.33	0.43	0.55
PCB #189	< 0.11	< 0.11	0.22	0.30	0.49	0.63
TEQ excl. LOD	0.0017	0.0030	0.0033	0.0060	0.017	0.013
TEQ ½ LOD	0.0017	0.0031	0.0034	0.0060	0.017	0.013
TEQ incl. LOD	0.0018	0.0032	0.0035	0.0060	0.017	0.013
PCDD/PCDF homologues	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)
TCDD	< 2.3	< 2.3	< 2.3	4.8	12	9.0
PCDD	< 3.3	< 3.3	< 3.3	6.4	11	19
HxCDD	< 9.1	< 9.1	< 9.1	16	40	51
HpCDD	< 23	< 23	< 23	37	85	133
OCDD	< 63	< 63	< 63	146	274	626
TCDF	< 26	< 26	< 26	< 26	61	90
PCDF	17	< 13	< 13	20	57	70
HxCDF	15	12	14	18	53	68
HpCDF	< 8.1	< 8.1	< 8.1	9.6	41	40
OCDF	< 17	< 17	< 17	< 17	24	33
PCDD/PCDF congeners	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)
2,3,7,8-TCDD	< 0.73	< 0.59	< 0.59	< 0.62	0.82	< 0.58
1,2,3,7,8-PeCDD	< 0.54	< 0.57	< 0.24	0.73	1.3	0.48
1,2,3,4,7,8-HxCDD	< 0.47	< 0.41	< 0.25	0.73	0.94	1.0
1,2,3,6,7,8-HxCDD	< 0.44	0.75	< 0.52	2.2	2.9	4.1
1,2,3,7,8,9-HxCDD	< 0.42	< 0.41	< 0.30	0.92	2.2	2.3
1,2,3,4,6,7,8-HpCDD	< 12	< 12	< 12	18	44	65
2,3,7,8-TCDF	2.2	0.91	0.89	2.0	3.7	5.0
1,2,3,7,8-PeCDF	1.1	0.63	0.42	1.6	5.0	4.8
2,3,4,7,8-PeCDF	1.6	0.64	0.58	1.5	4.6	4.8
1,2,3,4,7,8-HxCDF	1.4	0.38	0.98	1.5	5.6	6.1
1,2,3,6,7,8-HxCDF	< 0.40	< 0.28	0.50	1.3	5.8	6.1
1,2,3,7,8,9-HxCDF	< 0.94	< 0.36	< 0.39	< 0.61	1.5	2.3
2,3,4,6,7,8-HxCDF	4.5	3.3	4.1	3.9	8.9	9.7
1,2,3,4,6,7,8-HpCDF	< 4.3	<4.3	< 4.3	6.4	25	23
1,2,3,4,7,8,9-HpCDF	< 0.76		< 0.17	1.3	5.6	5.0
TEQ excl. LOD	1.3	0.74	0.84	2.8	7.6	6.8
TEQ ½ LOD	2.2	1.5	1.4	3.1	7.6	7.1
TEQ incl. LOD	3.1	2.2	2.0	3.5	7.6	7.4

Table S 18 Congener and homologue specific concentrations of PCBs and PCDD/PCDFs in U3

U3	<2000 µm >1000µm	<1000 µm >500 µm	<500 µm >250µm	<250 µm >125µm	<125 µm >63 µm	< 63 µm
PCB homologues	**(µg//kg)**	**(µg//kg)**	**(µg//kg)**	**(µg//kg)**	**(µg//kg)**	**(µg//kg)**
TriPCBs	< 8.2	< 8.2	< 8.2	11	< 8.2	8.5
TetraPCBs	< 16	< 16	< 16	27	17	23
PentaPCBs	< 27	< 27	< 27	54	32	37
HexaPCBs	< 36	< 36	< 36	64	46	50
HeptaPCBs	< 12	< 12	< 12	24	26	23
OctaPCBs	< 2.8	< 2.8	< 2.8	3.4	3.5	3.0
NonaPCBs	0.15	< 0.043	< 0.043	< 0.043	0.11	0.23
DecaPCB	< 0.11	< 0.11	< 0.11	< 0.11	< 0.11	0.16
PCB congeners	(µg//kg)	(µg//kg)	(µg//kg)	(µg//kg)	(µg//kg)	(µg//kg)
PCB #28	< 1.2	< 1.2	< 1.2	1.7	1.3	2.0
PCB #52	< 1.6	< 1.6	< 1.6	3.6	1.9	2.2
PCB #101	< 7.1	< 7.1	< 7.1	11	7.1	7.1
PCB #153	< 7.3	< 7.3	< 7.3	11	7.8	8.8
PCB #138	< 7.9	< 7.9	< 7.9	14	10	11
PCB #180	< 4.3	< 4.3	< 4.3	4.3	6.8	6.0
PCB #81	< 0.036	0.037	< 0.036	0.12	0.19	0.095
PCB #77	< 0.16	< 0.16	< 0.16	0.39	0.58	0.45
PCB #126	< 0.012	< 0.012	0.013	0.11	0.19	0.056
PCB #169	< 0.0041	< 0.0041	< 0.0041	0.014	< 0.0041	0.0072
PCB #123	< 0.23	< 0.23	< 0.23	0.59	0.36	0.37
PCB #118	< 2.4	< 2.4	< 2.4	4.1	3.0	3.9
PCB #114	< 0.075	< 0.075	< 0.075	0.093	0.24	0.085
PCB #105	< 0.64	< 0.64	< 0.64	1.3	1.1	1.6
PCB #167	< 0.35	< 0.35	< 0.35	0.54	0.46	0.48
PCB #156	< 0.69	< 0.69	< 0.69	1.1	0.86	0.95
PCB #157	< 0.22	< 0.22	< 0.22	0.28	< 0.22	< 0.22
PCB #189	< 0.11	< 0.11	< 0.11	0.15	0.18	0.20
TEQ excl. LOD			0.0013	0.0090	0.0039	0.0061
TEQ ½ LOD	0.00076	0.00077	0.0014	0.0090	0.0040	0.0061
TEQ incl. LOD	0.0015	0.0015	0.0015	0.0090	0.0040	0.0061
PCDD/PCDF homologues	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)
TCDD	< 2.3	< 2.3	4.0	6.2	11	23
PCDD	< 3.3	< 3.3	< 3.3	4.2	11	13
HxCDD	< 9.1	< 9.1	< 9.1	< 9.1	< 9.1	23
HpCDD	< 23	< 23	< 23	< 23	< 23	< 23
OCDD	87	< 63	< 63	< 63	< 63	< 63
TCDF	< 26	< 26	< 26	< 26	< 26	30
PCDF	< 13	< 13	< 13	< 13	16	21
HxCDF	< 10	< 10	< 10	11	< 10	15
HpCDF	< 8.1	< 8.1	< 8.1	< 8.1	< 8.1	10
OCDF	< 17	< 17	< 17	< 17	< 17	< 17
PCDD/PCDF congeners	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)
2,3,7,8-TCDD	0.24	0.50	0.49	0.36	1.1	1.2
1,2,3,7,8-PeCDD	0.22	0.12	0.20	0.28	< 1.2	1.3
1,2,3,4,7,8-HxCDD	0.18	0.081	0.21	0.28	0.56	1.7
1,2,3,6,7,8-HxCDD	0.16	0.26	0.29	0.52	0.58	2.5
1,2,3,7,8,9-HxCDD	0.16	0.065	0.20	0.32	0.52	4.4
1,2,3,4,6,7,8-HpCDD	< 12	< 12	< 12	< 12	< 12	< 12
2,3,7,8-TCDF	< 0.47	< 0.73	< 0.37	1.4	1.2	2.3
1,2,3,7,8-PeCDF	< 0.16	< 0.29	< 0.26	0.83	0.66	2.1
2,3,4,7,8-PeCDF	< 0.16	< 0.18	< 0.22	0.81	0.63	1.3
1,2,3,4,7,8-HxCDF	< 0.062	< 0.12	< 0.39	0.89	< 0.65	1.5
1,2,3,6,7,8-HxCDF	< 0.059	< 0.11	< 0.27	0.51	< 0.53	0.75
1,2,3,7,8,9-HxCDF	< 0.15	< 0.061	< 0.22	< 0.12	< 0.83	0.29
2,3,4,6,7,8-HxCDF	2.1	2.4	2.5	2.7	2.6	3.0
1,2,3,4,6,7,8-HpCDF	< 4.3	< 4.3	< 4.3	< 4.3	< 4.3	7.8
1,2,3,4,7,8,9-HpCDF	< 0.055	< 0.28	< 0.32	< 0.21	< 0.93	< 0.96
TEQ excl. LOD	0.75	0.89	1.0	1.6	1.9	2.7
TEQ ½ LOD	0.90	1.1	1.2	1.7	2.6	2.8
TEQ incl. LOD	1.0	1.3	1.4	1.8	3.4	2.9

Table S 19 Congener and homologue specific concentrations of PCBs and PCDD/PCDFs in U4

U4	<2000 µm >1000µm	<1000 µm >500 µm	<500 µm >250µm	<250 µm >125µm	<125 µm >63 µm	< 63 µm
PCB homologues	**(µg//kg)**	**(µg//kg)**	**(µg//kg)**	**(µg//kg)**	**(µg//kg)**	**(µg//kg)**
TriPCBs	14	< 8.2	24	< 8.2	27	17
TetraPCBs	23	< 16	17	17	40	29
PentaPCBs	< 27	< 27	< 27	45	101	120
HexaPCBs	142	< 36	41	82	181	257
HeptaPCBs	12	< 12	13	34	12	158
OctaPCBs	< 2.8	< 2.8	< 2.8	4.3	16	20
NonaPCBs	< 0.043	< 0.043	< 0.043	< 0.043	< 0.043	< 0.043
DecaPCB	0.30	< 0.11	< 0.11	0.45	< 0.11	< 0.11
PCB congeners	(µg//kg)	(µg//kg)	(µg//kg)	(µg//kg)	(µg//kg)	(µg//kg)
PCB #28	3.4	1.7	2.0	1.2	3.0	2.6
PCB #52	2.4	1.6	1.8	2.0	4.3	4.4
PCB #101	< 7.1	< 7.1	< 7.1	10	21	26
PCB #153	25	< 7.3	< 7.3	13	33	48
PCB #138	< 7.9	< 7.9	< 7.9	17	41	62
PCB #180	< 4.3	< 4.3	< 4.3	8.7	30	42
PCB #81	0.063	0.051	0.052	0.37	0.17	0.20
PCB #77	0.27	0.22	0.21	0.62	0.63	0.61
PCB #126	0.029	0.027	0.019	0.071	0.11	0.082
PCB #169	0.010	0.0050	< 0.0041	0.0067	0.015	0.012
PCB #123	0.35	< 0.23	0.50	0.53	1.2	1.3
PCB #118	2.7	< 2.4	2.6	3.4	9.6	9.4
PCB #114	0.18	0.14	< 0.075	0.094	0.19	0.098
PCB #105	0.97	0.74	0.78	0.96	2.7	2.5
PCB #167	< 0.35	< 0.35	< 0.35	0.65	1.8	2.3
PCB #156	< 0.69	< 0.69	< 0.69	1.4	3.7	5.2
PCB #157	< 0.22	< 0.22	< 0.22	0.28	0.76	0.75
PCB #189	0.16	0.14	0.12	0.19	0.47	0.72
TEQ excl. LOD	0.0034	0.0029	0.0021	0.0077	0.012	0.0094
TEQ ½ LOD	0.0034	0.0030	0.0021	0.0077	0.012	0.0094
TEQ incl. LOD	0.0035	0.0030	0.0022	0.0077	0.012	0.0094
PCDD/PCDF homologues	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)
TCDD	< 2.3	4.0	< 2.3	9.4	10	14
PCDD	< 3.3	11	< 3.3	17	13	15
HxCDD	< 9.1	< 9.1	< 9.1	67	54	65
HpCDD	< 23	< 23	< 23	172	134	165
OCDD	< 63	< 63	< 63	419	320	399
TCDF	< 26	< 26	< 26	99	45	71
PCDF	< 13	< 13	< 13	81	43	48
HxCDF	< 10	< 10	< 10	49	38	47
HpCDF	< 8.1	< 8.1	< 8.1	33	32	39
OCDF	< 17	< 17	< 17	31	26	34
PCDD/PCDF congeners	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)
2,3,7,8-TCDD	< 0.58	< 0.61	< 1.1	0.73	< 1.1	1.6
1,2,3,7,8-PeCDD	< 1.2	< 0.75	< 0.85	0.54	< 1.0	0.70
1,2,3,4,7,8-HxCDD	< 0.68	< 0.19	< 0.95	0.71	< 1.6	2.0
1,2,3,6,7,8-HxCDD	< 0.58	< 0.18	0.54	2.7	3.3	2.6
1,2,3,7,8,9-HxCDD	< 0.64	< 0.64	< 0.44	1.2	1.3	1.9
1,2,3,4,6,7,8-HpCDD	< 12	< 12	< 12	74	62	71
2,3,7,8-TCDF	< 0.57	1.1	1.5	10	6.0	5.7
1,2,3,7,8-PeCDF	< 0.33	< 0.22	0.68	5.1	2.4	4.3
2,3,4,7,8-PeCDF	< 0.63	0.44	0.87	10	4.6	3.8
1,2,3,4,7,8-HxCDF	< 0.18	0.50	0.66	7.0	4.6	5.8
1,2,3,6,7,8-HxCDF	< 0.15	0.24	0.65	2.6	2.0	4.4
1,2,3,7,8,9-HxCDF	< 0.72	< 0.46	< 0.47	0.56	0.68	1.5
2,3,4,6,7,8-HxCDF	< 4.6	3.8	3.9	5.5	4.5	6.8
1,2,3,4,6,7,8-HpCDF	< 4.3	< 4.3	< 4.3	19	20	23
1,2,3,4,7,8,9-HpCDF	< 0.90	< 0.70	< 0.90	1.8	< 1.5	2.3
TEQ excl. LOD	0.46	0.70	1.0	8.6	4.6	7.8
TEQ ½ LOD	1.7	1.6	2.2	8.6	5.7	7.8
TEQ incl. LOD	2.9	2.4	3.3	8.6	6.9	7.8

Table S 20 Congener and homologue specific concentrations of PCBs and PCDD/PCDFs in U5

U5	<2000 µm >1000µm	<1000 µm >500 µm	<500 µm >250µm	<250 µm >125µm	<125 µm >63 µm	< 63 µm
PCB homologues	**(µg//kg)**	**(µg//kg)**	**(µg//kg)**	**(µg//kg)**	**(µg//kg)**	**(µg//kg)**
TriPCBs	< 8.2	< 8.2	< 8.2	8.8	13	22
TetraPCBs	< 16	< 16	< 16	19	33	47
PentaPCBs	< 27	< 27	< 27	31	56	77
HexaPCBs	< 36	< 36	< 36	< 36	91	132
HeptaPCBs	< 12	< 12	< 12	18	47	78
OctaPCBs	< 2.8	< 2.8	< 2.8	< 2.8	5.6	10
NonaPCBs	< 0.043	< 0.043	< 0.043	< 0.043	< 0.043	0.42
DecaPCB	0.27	0.16	0.12	0.12	0.13	0.18
PCB congeners	(µg//kg)	(µg//kg)	(µg//kg)	(µg//kg)	(µg//kg)	(µg//kg)
PCB #28	1.5	1.5	1.4	1.8	2.5	3.6
PCB #52	< 1.6	< 1.6	< 1.6	2.1	3.1	4.0
PCB #101	< 7.1	< 7.1	< 7.1	< 7.1	11	15
PCB #153	< 7.3	< 7.3	< 7.3	< 7.3	16	23
PCB #138	< 7.9	< 7.9	< 7.9	8.8	21	30
PCB #180	< 4.3	< 4.3	< 4.3	4.6	12	20
PCB #81	< 0.036	< 0.036	< 0.036	0.064	0.12	0.16
PCB #77	< 0.16	< 0.16	0.21	0.30	0.51	0.73
PCB #126	< 0.012	< 0.012	0.019	0.025	0.080	0.11
PCB #169	< 0.0041	< 0.0041	< 0.0041	0.0022	0.0080	0.014
PCB #123	0.28	< 0.23	0.34	0.42	0.69	0.99
PCB #118	< 2.4	< 2.4	< 2.4	2.9	5.3	7.6
PCB #114	0.14	< 0.075	0.12	0.13	0.20	0.12
PCB #105	< 0.64	< 0.64	0.70	1.2	2.0	2.6
PCB #167	< 0.35	< 0.35	< 0.35	< 0.35	0.83	1.3
PCB #156	< 0.69	< 0.69	< 0.69	0.72	1.9	3.0
PCB #157	< 0.22	< 0.22	< 0.22	< 0.22	0.42	0.50
PCB #189	< 0.11	< 0.11	< 0.11	< 0.11	0.69	0.36
TEQ excl. LOD			0.0015	0.0028	0.0087	0.012
TEQ ½ LOD	0.00077	0.00076	0.0016	0.0028	0.0087	0.012
TEQ incl. LOD	0.0015	0.0015	0.0017	0.0028	0.0087	0.012
PCDD/PCDF homologues	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)
TCDD	< 2.3	3.0	3.9	6.2	6.6	9.3
PCDD	< 3.3	6.2	8.0	7.7	11	14
HxCDD	11	15	17	21	30	34
HpCDD	< 23	< 23	< 23	44	45	64
OCDD	< 63	< 63	< 63	130	138	191
TCDF	< 26	< 26	< 26	27	40	58
PCDF	< 13	< 13	< 13	< 13	28	42
HxCDF	< 10	< 10	< 10	20	25	39
HpCDF	< 8.1	< 8.1	< 8.1	20	22	28
OCDF	< 17	< 17	< 17	28	28	34
PCDD/PCDF congeners	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)
2,3,7,8-TCDD	< 0.087	< 0.083	< 0.12	< 0.75	< 0.83	< 0.97
1,2,3,7,8-PeCDD	< 0.076	< 0.16	< 0.27	0.48	0.33	0.55
1,2,3,4,7,8-HxCDD	< 0.053	0.25	< 0.074	< 0.27	0.93	0.51
1,2,3,6,7,8-HxCDD	0.15	< 0.057	0.49	0.76	0.93	2.3
1,2,3,7,8,9-HxCDD	< 0.055	< 0.24	0.23	< 0.063	0.72	1.4
1,2,3,4,6,7,8-HpCDD	< 12	< 12	< 12	26	23	33
2,3,7,8-TCDF	0.52	0.56	0.69	1.2	2.2	3.2
1,2,3,7,8-PeCDF	0.22	0.28	0.40	1.1	2.0	3.3
2,3,4,7,8-PeCDF	< 0.038	< 0.055	0.38	0.89	1.7	3.0
1,2,3,4,7,8-HxCDF	0.50	0.33	0.62	1.8	2.2	4.6
1,2,3,6,7,8-HxCDF	< 0.080	0.36	0.27	1.4	1.2	2.7
1,2,3,7,8,9-HxCDF	< 0.12	< 0.071	< 0.11	0.36	0.81	0.73
2,3,4,6,7,8-HxCDF	3.0	2.6	3.2	3.1	3.9	5.7
1,2,3,4,6,7,8-HpCDF	< 4.3	< 4.3	< 4.3	13	12	17
1,2,3,4,7,8,9-HpCDF	< 0.089	< 0.56	< 0.29	1.8	1.1	1.5
TEQ excl. LOD	0.43	0.42	0.68	2.1	2.6	4.2
TEQ ½ LOD	0.62	0.66	0.98	2.5	3.0	4.7
TEQ incl. LOD	0.82	0.91	1.3	2.9	3.4	5.2

Table S 21 Congener and homologue specific concentrations of PCBs and PCDD/PCDFs in U6

U6	<2000 µm >1000µm	<1000 µm >500 µm	<500 µm >250µm	<250 µm >125µm	<125 µm >63 µm	< 63 µm
PCB homologues	**(µg//kg)**	**(µg//kg)**	**(µg//kg)**	**(µg//kg)**	**(µg//kg)**	**(µg//kg)**
TriPCBs	< 8.2	< 8.2	14	14	33	43
TetraPCBs	< 16	23	19	34	66	75
PentaPCBs	34	159	41	126	161	145
HexaPCBs	51	432	93	277	287	274
HeptaPCBs	22	241	62	160	162	138
OctaPCBs	3.2	34	8.4	21	21	17
NonaPCBs	< 0.043	0.98	< 0.043	< 0.043	0.71	1.8
DecaPCB	< 0.11	0.16	0.27	< 0.11	0.15	0.11
PCB congeners	(µg//kg)	(µg//kg)	(µg//kg)	(µg//kg)	(µg//kg)	(µg//kg)
PCB #28	< 1.2	1.3	1.5	2.2	4.4	6.3
PCB #52	< 1.6	4.4	2.0	4.7	5.9	7.3
PCB #101	< 7.1	41	8.9	30	29	29
PCB #153	9.6	81	16	50	52	50
PCB #138	12	100	22	64	66	63
PCB #180	5.6	67	16	41	41	38
PCB #81	0.069	0.30	0.089	0.20	0.23	0.25
PCB #77	0.28	0.59	0.44	0.70	1.3	1.3
PCB #126	0.045	0.17	0.078	0.13	0.22	0.22
PCB #169	0.0051	0.017	0.0094	0.013	0.020	0.022
PCB #123	0.90	1.9	0.66	1.8	2.1	2.6
PCB #118	3.1	14	3.9	10	13	13
PCB #114	0.35	0.32	0.13	0.14	0.16	0.52
PCB #105	1.0	2.8	1.0	2.7	4.1	4.5
PCB #167	0.67	4.2	0.81	2.3	2.7	2.5
PCB #156	1.3	10	1.6	4.9	5.5	4.8
PCB #157	< 0.22	1.3	0.55	0.83	0.96	0.83
PCB #189	0.15	1.2	0.44	0.66	0.75	0.62
TEQ excl. LOD	0.0049	0.019	0.0085	0.014	0.024	0.024
TEQ ½ LOD	0.0049	0.019	0.0085	0.014	0.024	0.024
TEQ incl. LOD	0.0049	0.019	0.0085	0.014	0.024	0.024
PCDD/PCDF homologues	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)
TCDD	8.7	7.1	8.0	12	21	23
PCDD	12	9.8	19	9.8	22	25
HxCDD	23	45	47	52	86	80
HpCDD	< 23	157	82	134	244	217
OCDD	< 63	569	367	732	1182	1000
TCDF	40	63	56	95	165	204
PCDF	23	49	47	71	128	121
HxCDF	27	46	36	51	85	123
HpCDF	< 8.1	42	18	29	50	68
OCDF	< 17	52	22	35	38	61
PCDD/PCDF congeners	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)
2,3,7,8-TCDD	0.83	0.72	0.33	< 0.21	0.67	0.51
1,2,3,7,8-PeCDD	< 0.24	< 0.12	0.54	< 0.25	1.2	1.2
1,2,3,4,7,8-HxCDD	0.23	0.34	0.98	< 0.61	1.8	1.5
1,2,3,6,7,8-HxCDD	0.87	3.2	1.7	0.92	4.5	3.9
1,2,3,7,8,9-HxCDD	0.41	1.0	1.1	1.4	4.0	2.8
1,2,3,4,6,7,8-HpCDD	< 12	96	40	71	120	105
2,3,7,8-TCDF	2.0	3.9	3.4	6.8	12	9.8
1,2,3,7,8-PeCDF	1.5	3.0	2.8	4.4	8.7	8.0
2,3,4,7,8-PeCDF	1.7	3.5	3.3	5.3	8.1	9.9
1,2,3,4,7,8-HxCDF	1.5	4.1	2.9	6.0	8.6	9.6
1,2,3,6,7,8-HxCDF	1.1	1.8	2.3	4.2	6.8	9.4
1,2,3,7,8,9-HxCDF	0.25	0.79	0.58	0.69	1.5	2.1
2,3,4,6,7,8-HxCDF	4.6	4.4	4.3	5.1	7.6	11
1,2,3,4,6,7,8-HpCDF	5.4	18	12	20	35	42
1,2,3,4,7,8,9-HpCDF	0.68	1.6	< 0.39	1.3	2.9	7.8
TEQ excl. LOD	2.5	5.2	4.3	5.4	11	12
TEQ ½ LOD	2.7	5.2	4.3	5.6	11	12
TEQ incl. LOD	2.9	5.3	4.3	5.9	11	12

Table S 22 Congener and homologue specific concentrations of PCBs and PCDD/PCDFs in UI6

UI6	<2000 µm >1000µm	<1000 µm >500 µm	<500 µm >250µm	<250 µm >125µm	<125 µm >63 µm	< 63 µm
PCB homologues	**(µg//kg)**	**(µg//kg)**	**(µg//kg)**	**(µg//kg)**	**(µg//kg)**	**(µg//kg)**
TriPCBs		9.4	< 8.2	< 8.2	< 8.2	< 8.2
TetraPCBs		34	< 16	< 16	< 16	< 16
PentaPCBs		88	< 27	< 27	< 27	< 27
HexaPCBs		83	< 36	< 36	< 36	< 36
HeptaPCBs		22	< 12	< 12	< 12	< 12
OctaPCBs		< 2.8	< 2.8	< 2.8	< 2.8	< 2.8
NonaPCBs		< 0.043	< 0.043	< 0.043	< 0.043	< 0.043
DecaPCB		< 0.11	< 0.11	< 0.11	< 0.11	< 0.11
PCB congeners	(µg//kg)	(µg//kg)	(µg//kg)	(µg//kg)	(µg//kg)	(µg//kg)
PCB #28		1.8	< 1.2	< 1.2	< 1.2	< 1.2
PCB #52		4.0	< 1.6	< 1.6	1.9	< 1.6
PCB #101		14	< 7.1	< 7.1	< 7.1	< 7.1
PCB #153		14	< 7.3	< 7.3	< 7.3	< 7.3
PCB #138		21	< 7.9	< 7.9	< 7.9	< 7.9
PCB #180		6.1	< 4.3	< 4.3	< 4.3	< 4.3
PCB #81		0.22	0.038	< 0.036	0.060	< 0.036
PCB #77		0.54	< 0.16	< 0.16	0.19	< 0.16
PCB #126		0.046	< 0.012	< 0.012	0.029	0.017
PCB #169		< 0.0041	< 0.0041	< 0.0041	< 0.0041	< 0.0041
PCB #123		< 0.29	< 0.23	< 0.23	< 0.23	< 0.23
PCB #118		11	< 2.4	< 2.4	2.5	< 2.4
PCB #114		0.21	< 0.075	< 0.075	< 0.075	< 0.075
PCB #105		4.7	< 0.64	< 0.64	1.1	< 0.64
PCB #167		0.98	< 0.35	< 0.35	< 0.35	< 0.35
PCB #156		2.0	< 0.69	< 0.69	< 0.69	< 0.69
PCB #157		0.29	< 0.22	< 0.22	< 0.22	< 0.22
PCB #189		0.16	< 0.11	< 0.11	< 0.11	< 0.11
TEQ excl. LOD		0.0053		0.014	0.0030	0.0017
TEQ ½ LOD		0.0054	0.00077	0.00076	0.0031	0.0018
TEQ incl. LOD		0.0055	0.0015	0.0015	0.0032	0.0020
PCDD/PCDF homologues		(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)
TCDD		54	< 2.3	< 2.3	4.5	3.5
PCDD		247	< 3.3	< 3.3	6.0	8.0
HxCDD		1443	< 9.1	< 9.1	16	11
HpCDD		942	< 23	< 23	< 23	< 23
OCDD		549	< 63	< 63	< 63	< 63
TCDF		149	< 26	< 26	69	45
PCDF		163	< 13	18	58	35
HxCDF		117	13	18	43	33
HpCDF		47	< 8.1	< 8.1	15	12
OCDF		< 17	< 17	< 17	< 17	< 17
PCDD/PCDF congeners	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)
2,3,7,8-TCDD		0.90	< 0.11	< 1.2	< 0.56	0.41
1,2,3,7,8-PeCDD		2.8	< 0.19	< 0.39	0.54	0.47
1,2,3,4,7,8-HxCDD		5.6	< 0.13	< 0.41	0.50	0.42
1,2,3,6,7,8-HxCDD		38	< 0.14	< 0.35	1.2	0.87
1,2,3,7,8,9-HxCDD		16	< 0.28	< 0.37	0.49	0.47
1,2,3,4,6,7,8-HpCDD		429	< 12	< 12	< 12	12
2,3,7,8-TCDF		11	1.5	< 1.0	2.7	1.4
1,2,3,7,8-PeCDF		18	0.89	1.4	4.8	3.2
2,3,4,7,8-PeCDF		16	1.3	1.2	4.3	1.9
1,2,3,4,7,8-HxCDF		15	0.84	1.6	3.7	2.2
1,2,3,6,7,8-HxCDF		10	0.61	1.0	2.9	2.8
1,2,3,7,8,9-HxCDF		< 3.0	< 0.35	0.54	0.69	0.91
2,3,4,6,7,8-HxCDF		17	5.0	5.0	6.5	6.8
1,2,3,4,6,7,8-HpCDF		45	< 4.3	< 4.3	12	7.7
1,2,3,4,7,8,9-HpCDF		< 8.3	< 0.93	< 1.3	0.80	1.5
TEQ excl. LOD		25	1.2	1.2	4.0	2.8
TEQ ½ LOD		25	1.5	2.2	4.3	3.1
TEQ incl. LOD		26	1.8	3.2	4.7	3.4

Table S 23 Congener and homologue specific concentrations of PCBs and PCDD/PCDFs in UI7

UI7	<2000 µm >1000µm	<1000 µm >500 µm	<500 µm >250µm	<250 µm >125µm	<125 µm >63 µm	< 63 µm
PCB homologues	**(µg//kg)**	**(µg//kg)**	**(µg//kg)**	**(µg//kg)**	**(µg//kg)**	**(µg//kg)**
TriPCBs	< 8.2	< 8.2	< 8.2	< 8.2	< 8.2	8.3
TetraPCBs	< 16	< 16	< 16	34	33	44
PentaPCBs	< 27	< 27	42	37	43	54
HexaPCBs	46	< 36	108	67	88	94
HeptaPCBs	18	14	56	34	44	46
OctaPCBs	< 2.8	2.9	8.1	5.1	7.2	7.6
NonaPCBs	< 0.043	0.50	0.26	0.46	0.67	0.46
DecaPCB	< 0.11	0.20	< 0.11	0.17	0.21	0.15
PCB congeners	(µg//kg)	(µg//kg)	(µg//kg)	(µg//kg)	(µg//kg)	(µg//kg)
PCB #28	< 1.2	< 1.2	< 1.2	1.5	1.3	1.9
PCB #52	< 1.6	< 1.6	< 1.6	1.8	2.1	2.3
PCB #101	< 7.1	< 7.1	9.6	< 7.1	< 7.1	9.3
PCB #153	7.9	7.3	20	12	16	18
PCB #138	10	7.9	26	16	21	24
PCB #180	5.0	4.3	17	9.9	13	14
PCB #81	0.055	0.059	0.085	0.095	0.12	0.14
PCB #77	0.30	0.41	0.44	0.79	0.87	1.1
PCB #126	0.055	0.060	0.081	0.13	0.13	0.16
PCB #169	0.0064	0.010	0.011	0.023	0.020	0.024
PCB #123	< 0.23	< 0.23	0.53	0.47	0.53	0.67
PCB #118	2.9	< 2.4	3.9	4.4	5.4	6.7
PCB #114	< 0.075	< 0.075	0.10	0.12	0.19	0.26
PCB #105	1.2	0.93	1.3	2.4	2.7	3.3
PCB #167	0.42	< 0.35	1.2	0.80	0.98	1.1
PCB #156	0.89	< 0.69	2.2	1.6	1.8	2.1
PCB #157	< 0.22	0.27	0.33	0.29	0.35	0.41
PCB #189	0.15	0.12	0.50	0.30	0.39	0.40
TEQ excl. LOD	0.0059	0.0064	0.0088	0.014	0.014	0.017
TEQ ½ LOD	0.0059	0.0064	0.0088	0.014	0.014	0.017
TEQ incl. LOD	0.0059	0.0065	0.0088	0.014	0.014	0.017
PCDD/PCDF homologues	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)
TCDD	12	8.8	11	39	30	44
PCDD	20	12	12	73	54	73
HxCDD	35	29	44	172	120	159
HpCDD	36	25	28	245	123	182
OCDD	73	63	63	439	145	198
TCDF	201	85	94	501	356	542
PCDF	125	77	84	578	412	557
HxCDF	89	59	79	540	320	520
HpCDF	41	28	35	255	146	230
OCDF	21	< 17	29	83	58	81
PCDD/PCDF congeners	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)
2,3,7,8-TCDD	0.46	0.41	0.62	1.6	0.83	1.2
1,2,3,7,8-PeCDD	0.90	0.53	1.8	4.5	3.2	4.2
1,2,3,4,7,8-HxCDD	0.91	0.57	3.0	4.8	3.3	4.2
1,2,3,6,7,8-HxCDD	2.2	1.2	4.0	12	7.4	10
1,2,3,7,8,9-HxCDD	1.9	1.1	3.9	9.5	5.9	10
1,2,3,4,6,7,8-HpCDD	18	13	15	122	62	90
2,3,7,8-TCDF	6.6	2.1	3.4	14	9.0	18
1,2,3,7,8-PeCDF	10	6.5	7.0	51	33	48
2,3,4,7,8-PeCDF	10	4.3	6.8	34	22	32
1,2,3,4,7,8-HxCDF	8.4	4.6	7.0	43	26	42
1,2,3,6,7,8-HxCDF	7.4	7.6	11	78	42	67
1,2,3,7,8,9-HxCDF	2.1	2.1	5.7	24	11	21
2,3,4,6,7,8-HxCDF	12	11	15	82	47	71
1,2,3,4,6,7,8-HpCDF	27	18	22	171	97	155
1,2,3,4,7,8,9-HpCDF	3.8	4.6	9.8	43	25	37
TEQ excl. LOD	9.4	5.8	10	48	29	44
TEQ ½ LOD	9.4	5.8	10	48	29	44
TEQ incl. LOD	9.4	5.8	10	48	29	44

Table S 24 Congener and homologue specific concentrations of PCBs and PCDD/PCDFs in UI8

UI8	<2000 µm >1000µm	<1000 µm >500 µm	<500 µm >250µm	<250 µm >125µm	<125 µm >63 µm	< 63 µm
PCB homologues	**(µg//kg)**	**(µg//kg)**	**(µg//kg)**	**(µg//kg)**	**(µg//kg)**	**(µg//kg)**
TriPCBs	< 8.2	< 8.2	8.3	18	24	25
TetraPCBs	33	39	36	88	101	95
PentaPCBs	69	82	82	225	252	231
HexaPCBs	83	112	111	315	364	324
HeptaPCBs	37	52	47	156	178	166
OctaPCBs	3.6	5.6	5.0	19	23	21
NonaPCBs	< 0.043	< 0.043	0.11	0.59	0.69	0.72
DecaPCB	< 0.11	0.23	< 0.11	< 0.11	0.13	0.12
PCB congeners	(µg//kg)	(µg//kg)	(µg//kg)	(µg//kg)	(µg//kg)	(µg//kg)
PCB #28	1.5	1.9	2.1	4.2	5.3	5.7
PCB #52	2.7	2.7	2.4	5.8	6.5	6.1
PCB #101	13	14	13	34	37	35
PCB #153	18	22	21	59	68	61
PCB #138	21	27	28	84	96	84
PCB #180	9.2	13	14	46	53	49
PCB #81	0.17	0.18	0.20	0.55	0.60	0.55
PCB #77	0.71	0.89	1.1	3.4	3.9	3.6
PCB #126	0.10	0.15	0.20	0.72	0.85	0.77
PCB #169	0.0063	0.013	0.014	0.061	0.069	0.063
PCB #123	0.59	0.66	0.76	2.0	2.0	1.8
PCB #118	8.5	11	11	32	36	32
PCB #114	0.25	0.31	0.33	0.85	0.95	0.80
PCB #105	3.2	4.7	4.9	14	17	16
PCB #167	0.81	1.2	1.2	3.9	4.4	3.9
PCB #156	1.5	2.3	2.2	7.8	8.6	7.9
PCB #157	0.59	0.51	0.57	1.6	1.6	1.6
PCB #189	0.21	0.24	0.28	0.98	1.2	1.1
TEQ excl. LOD	0.011	0.017	0.022	0.077	0.090	0.082
TEQ ½ LOD	0.011	0.017	0.022	0.077	0.090	0.082
TEQ incl. LOD	0.011	0.017	0.022	0.077	0.090	0.082
PCDD/PCDF homologues	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)
TCDD	13	109	119	405	490	420
PCDD	14	90	85	312	325	297
HxCDD	37	61	59	179	207	197
HpCDD	30	27	29	96	125	124
OCDD	< 63	26	45	85	96	95
TCDF	104	85	94	501	356	542
PCDF	88	77	84	578	412	557
HxCDF	65	59	79	540	320	520
HpCDF	32	28	35	255	146	230
OCDF	< 17	< 17	29	83	58	81
PCDD/PCDF congeners	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)
2,3,7,8-TCDD	0.47	0.43	0.29	1.6	1.9	0.93
1,2,3,7,8-PeCDD	0.60	1.7	1.1	3.8	2.9	2.2
1,2,3,4,7,8-HxCDD	0.61	2.8	0.67	2.2	2.5	1.8
1,2,3,6,7,8-HxCDD	1.3	3.2	1.0	4.3	7.1	4.3
1,2,3,7,8,9-HxCDD	1.6	2.8	0.81	4.4	6.4	4.9
1,2,3,4,6,7,8-HpCDD	12	14	15	52	83	67
2,3,7,8-TCDF	4.8	6.4	7.0	26	34	31
1,2,3,7,8-PeCDF	7.2	6.0	6.5	23	27	24
2,3,4,7,8-PeCDF	4.7	5.7	5.6	19	23	21
1,2,3,4,7,8-HxCDF	6.1	6.0	6.0	20	23	23
1,2,3,6,7,8-HxCDF	5.5	5.8	5.0	16	18	20
1,2,3,7,8,9-HxCDF	2.2	3.0	1.7	5.1	4.4	5.5
2,3,4,6,7,8-HxCDF	11	8.7	7.3	16	18	19
1,2,3,4,6,7,8-HpCDF	21	18	20	63	77	77
1,2,3,4,7,8,9-HpCDF	2.7	5.0	3.0	9.7	12	14
TEQ excl. LOD	6.4	8.2	6.6	22	26	23
TEQ ½ LOD	6.4	8.2	6.6	22	26	23
TEQ incl. LOD	6.4	8.2	6.6	22	26	23

Table S 25 Congener and homologue specific concentrations of PCBs and PCDD/PCDFs in R1

R1	<2000 µm >1000µm	<1000 µm >500 µm	<500 µm >250µm	<250 µm >125µm	<125 µm >63 µm	< 63 µm
PCB homologues	**(µg//kg)**	**(µg//kg)**	**(µg//kg)**	**(µg//kg)**	**(µg//kg)**	**(µg//kg)**
TriPCBs	< 8.2	< 8.2	< 8.2	< 8.2	< 8.2	< 8.2
TetraPCBs	< 16	< 16	< 16	< 16	< 16	< 16
PentaPCBs	< 27	< 27	< 27	60	37	30
HexaPCBs	< 36	< 36	< 36	168	94	65
HeptaPCBs	< 12	< 12	< 12	100	58	34
OctaPCBs	< 2.8	< 2.8	< 2.8	14	7.8	4.3
NonaPCBs	< 0.043	< 0.043	< 0.043	0.37	0.21	0.11
DecaPCB	< 0.11	< 0.11	< 0.11	< 0.11	< 0.11	< 0.11
PCB congeners	**(µg//kg)**	**(µg//kg)**	**(µg//kg)**	**(µg//kg)**	**(µg//kg)**	**(µg//kg)**
PCB #28	< 1.2	< 1.2	< 1.2	4.2	5.3	5.7
PCB #52	< 1.6	< 1.6	< 1.6	5.8	6.5	6.1
PCB #101	< 7.1	< 7.1	< 7.1	15	8.7	7.1
PCB #153	< 7.3	< 7.3	< 7.3	31	17	12
PCB #138	< 7.9	< 7.9	< 7.9	37	21	16
PCB #180	< 4.3	< 4.3	< 4.3	28	16	9.5
PCB #81	< 0.036	< 0.036	< 0.036	0.11	0.071	0.066
PCB #77	< 0.16	< 0.16	< 0.16	0.33	0.32	0.33
PCB #126	0.015	0.017	0.049	0.20	0.15	0.14
PCB #169	< 0.0041	< 0.0041	0.0056	0.022	0.020	0.020
PCB #123	< 0.23	< 0.23	< 0.23	0.73	0.46	0.32
PCB #118	< 2.4	< 2.4	< 2.4	4.6	3.1	3.1
PCB #114	< 0.075	< 0.075	< 0.075	< 0.075	< 0.075	< 0.075
PCB #105	< 0.64	< 0.64	< 0.64	1.0	0.88	0.97
PCB #167	< 0.35	< 0.35	< 0.35	1.6	1.0	0.75
PCB #156	< 0.69	< 0.69	< 0.69	3.2	1.9	1.3
PCB #157	< 0.22	< 0.22	< 0.22	0.46	0.33	< 0.22
PCB #189	< 0.11	< 0.11	< 0.11	0.72	0.43	0.22
TEQ excl. LOD	0.0015	0.0017	0.0049	0.021	0.016	0.015
TEQ ½ LOD	0.0017	0.0019	0.0051	0.021	0.016	0.015
TEQ incl. LOD	0.0018	0.0020	0.0053	0.021	0.016	0.015
PCDD/PCDF homologues	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)
TCDD	2.9	3.8	6.8	14	14	12
PCDD	3.3	3.8	6.6	13	18	18
HxCDD	< 9.1	< 9.1	12	24	30	35
HpCDD	< 23	< 23	< 23	36	39	50
OCDD	< 63	< 63	< 63	68	70	84
TCDF	< 26	< 26	29	57	60	62
PCDF	< 13	< 13	20	44	51	64
HxCDF	< 10	< 10	16	32	38	56
HpCDF	< 8.1	< 8.1	10	20	21	34
OCDF	< 17	< 17	< 17	18	20	25
PCDD/PCDF congeners	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)
2,3,7,8-TCDD	0.10	0.088	0.13	0.18	0.25	0.48
1,2,3,7,8-PeCDD	0.14	0.12	0.43	0.91	0.87	1.0
1,2,3,4,7,8-HxCDD	< 0.11	0.18	0.41	0.76	0.87	1.5
1,2,3,6,7,8-HxCDD	0.18	0.29	0.59	1.2	1.6	2.2
1,2,3,7,8,9-HxCDD	< 0.13	0.29	0.33	1.1	1.3	1.1
1,2,3,4,6,7,8-HpCDD	< 12	< 12	< 12	18	19	25
2,3,7,8-TCDF	0.77	0.75	1.4	3.3	4.0	3.6
1,2,3,7,8-PeCDF	0.57	0.84	2.2	3.5	4.7	6.3
2,3,4,7,8-PeCDF	0.48	0.49	1.1	3.2	3.5	4.3
1,2,3,4,7,8-HxCDF	0.66	0.77	1.9	4.6	5.5	7.5
1,2,3,6,7,8-HxCDF	0.47	0.74	1.4	2.6	3.4	4.7
1,2,3,7,8,9-HxCDF	< 0.16	0.11	0.24	0.57	0.60	1.8
2,3,4,6,7,8-HxCDF	1.6	1.4	1.9	3.3	4.0	5.8
1,2,3,4,6,7,8-HpCDF	< 4.3	< 4.3	6.7	14	14	21
1,2,3,4,7,8,9-HpCDF	< 0.29	< 0.25	0.79	1.7	2.7	4.2
TEQ excl. LOD	0.77	0.83	1.8	4.3	4.8	6.4
TEQ ½ LOD	0.89	0.92	1.9	4.3	4.8	6.4
TEQ incl. LOD	1.0	1.0	2.0	4.3	4.8	6.4

Table S 26 Congener and homologue specific concentrations of PCBs and PCDD/PCDFs in R2

R2	<2000 µm >1000µm	<1000 µm >500 µm	<500 µm >250µm	<250 µm >125µm	<125 µm >63 µm	< 63 µm
PCB homologues	**(µg//kg)**	**(µg//kg)**	**(µg//kg)**	**(µg//kg)**	**(µg//kg)**	**(µg//kg)**
TriPCBs	< 8.2	< 8.2	< 8.2	< 8.2	< 8.2	< 8.2
TetraPCBs	< 16	< 16	< 16	< 16	< 16	< 16
PentaPCBs	< 27	< 27	< 27	37	28	< 27
HexaPCBs	< 36	< 36	< 36	87	52	56
HeptaPCBs	< 12	< 12	< 12	46	27	31
OctaPCBs	< 2.8	< 2.8	< 2.8	5.8	3.5	3.7
NonaPCBs	< 0.043	< 0.043	< 0.043	0.13	< 0.043	< 0.043
DecaPCB	< 0.11	< 0.11	< 0.11	< 0.11	0.18	0.25
PCB congeners	(µg//kg)	(µg//kg)	(µg//kg)	(µg//kg)	(µg//kg)	(µg//kg)
PCB #28	< 1.2	< 1.2	< 1.2	< 1.2	< 1.2	< 1.2
PCB #52	< 1.6	< 1.6	< 1.6	< 1.6	< 1.6	< 1.6
PCB #101	< 7.1	< 7.1	< 7.1	9.7	< 7.1	< 7.1
PCB #153	< 7.3	< 7.3	< 7.3	15	9.5	11
PCB #138	< 7.9	< 7.9	< 7.9	20	12	13
PCB #180	< 4.3	< 4.3	< 4.3	12	7.5	7.9
PCB #81	< 0.036	< 0.036	< 0.036	0.071	0.045	0.056
PCB #77	< 0.16	< 0.16	< 0.16	0.19	0.21	0.27
PCB #126	0.017	0.025	0.038	0.13	0.13	0.14
PCB #169	< 0.0041	< 0.0041	< 0.0041	0.014	0.018	0.019
PCB #123	< 0.23	< 0.23	< 0.23	0.44	0.40	0.42
PCB #118	< 2.4	< 2.4	< 2.4	2.7	< 2.4	2.6
PCB #114	< 0.075	< 0.075	< 0.075	< 0.075	0.14	0.20
PCB #105	< 0.64	< 0.64	< 0.64	< 0.64	< 0.64	0.70
PCB #167	< 0.35	< 0.35	< 0.35	0.95	0.68	0.65
PCB #156	< 0.69	< 0.69	< 0.69	1.8	1.2	1.1
PCB #157	< 0.22	< 0.22	< 0.22	0.27	< 0.22	0.27
PCB #189	< 0.11	< 0.11	< 0.11	0.33	0.21	0.20
TEQ excl. LOD	0.0017	0.0025	0.0038	0.013	0.014	0.015
TEQ ½ LOD	0.0019	0.0026	0.0039	0.013	0.014	0.015
TEQ incl. LOD	0.0020	0.0027	0.0041	0.013	0.014	0.015
PCDD/PCDF homologues	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)
TCDD	< 2.3	3.8	2.6	2.6	3.4	< 2.3
PCDD	< 3.3	11	4.3	7.6	11	18
HxCDD	< 9.1	24	13	12	32	29
HpCDD	< 23	< 23	< 23	< 23	44	37
OCDD	< 63	< 63	< 63	< 63	105	83
TCDF	< 26	< 26	< 26	36	49	59
PCDF	< 13	< 13	19	29	45	50
HxCDF	< 10	< 10	22	26	42	46
HpCDF	< 8.1	< 8.1	23	22	36	38
OCDF	< 17	< 17	26	< 17	58	48
PCDD/PCDF congeners	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)
2,3,7,8-TCDD	0.096	< 0.12	< 0.21	< 0.29	< 0.26	< 1.3
1,2,3,7,8-PeCDD	0.26	0.38	0.25	0.54	< 0.34	1.6
1,2,3,4,7,8-HxCDD	< 0.080	0.56	0.34	< 0.64	0.62	< 0.82
1,2,3,6,7,8-HxCDD	< 0.094	1.6	0.76	0.98	2.0	2.4
1,2,3,7,8,9-HxCDD	< 0.13	1.1	0.62	< 0.32	1.4	2.0
1,2,3,4,6,7,8-HpCDD	< 12	13	< 12	< 12	22	16
2,3,7,8-TCDF	0.55	0.80	0.81	2.0	4.0	4.6
1,2,3,7,8-PeCDF	1.1	1.6	1.5	2.4	2.7	3.5
2,3,4,7,8-PeCDF	0.76	1.4	1.3	2.1	4.0	3.1
1,2,3,4,7,8-HxCDF	1.6	2.2	2.5	3.5	2.7	5.5
1,2,3,6,7,8-HxCDF	1.1	1.7	1.9	2.4	0.68	2.8
1,2,3,7,8,9-HxCDF	0.48	0.55	0.65	< 0.48	6.6	< 0.86
2,3,4,6,7,8-HxCDF	1.9	2.8	2.8	4.2	20	11
1,2,3,4,6,7,8-HpCDF	9.1	10	15	16	4.8	24
1,2,3,4,7,8,9-HpCDF	1.5	3.1	3.4	1.6	4.0	4.6
TEQ excl. LOD	1.3	2.2	1.9	2.7	3.5	5.9
TEQ ½ LOD	1.4	2.3	2.1	3.0	3.8	6.7
TEQ incl. LOD	1.5	2.4	2.3	3.3	4.1	7.4

Table S 27 Congener and homologue specific concentrations of PCBs and PCDD/PCDFs in I1

I1	<2000 µm >1000µm	<1000 µm >500 µm	<500 µm >250µm	<250 µm >125µm	<125 µm >63 µm	< 63 µm
PCB homologues	**(µg//kg)**	**(µg//kg)**	**(µg//kg)**	**(µg//kg)**	**(µg//kg)**	**(µg//kg)**
TriPCBs	413	634	1011	627	1386	945
TetraPCBs	809	1154	1377	1605	1659	1430
PentaPCBs	781	646	1020	881	951	738
HexaPCBs	376	492	941	670	573	406
HeptaPCBs	64	202	363	262	227	154
OctaPCBs	6.8	28	66	43	40	20
NonaPCBs	0.31	0.71	1.2	0.87	1.3	< 0.043
DecaPCB	< 0.11	0.15	< 0.11	0.38	0.27	0.38
PCB congeners	(µg//kg)	(µg//kg)	(µg//kg)	(µg//kg)	(µg//kg)	(µg//kg)
PCB #28	59	93	117	129	158	134
PCB #52	83	103	123	147	150	118
PCB #101	95	93	150	129	122	98
PCB #153	20	86	171	121	107	75
PCB #138	96	114	208	162	140	97
PCB #180	19	50	104	69	63	43
PCB #81	2.1	1.8	3.0	3.1	6.6	3.2
PCB #77	7.4	9.5	14	16	29	17
PCB #126	0.37	0.43	1.1	0.54	0.71	0.51
PCB #169	0.0092	0.016	0.037	0.042	0.097	0.091
PCB #123	4.7	6.3	10	15	13	9.8
PCB #118	123	85	143	114	109	92
PCB #114	4.1	3.4	4.3	0.63	5.9	5.8
PCB #105	61	42	57	64	58	47
PCB #167	4.6	4.9	8.2	8.8	7.2	4.8
PCB #156	12	11	19	14	13	10
PCB #157	3.4	2.4	3.7	4.9	4.7	3.3
PCB #189	0.59	1.2	3.5	3.4	1.3	1.2
TEQ excl. LOD	0.045	0.049	0.12	0.064	0.081	0.059
TEQ ½ LOD	0.045	0.049	0.12	0.064	0.083	0.060
TEQ incl. LOD	0.045	0.049	0.12	0.065	0.085	0.062
PCDD/PCDF homologues	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)
TCDD	10	24	15	20	28	34
PCDD	8.4	21	16	20	40	< 3.3
HxCDD	29	70	37	49	85	106
HpCDD	66	296	119	156	245	192
OCDD	228	925	439	488	722	521
TCDF	80	136	96	141	259	
PCDF	114	106	81	107	171	144
HxCDF	111	95	69	84	167	167
HpCDF	27	57	46	57	101	88
OCDF	286	392	54	49	437	80
PCDD/PCDF congeners	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)
2,3,7,8-TCDD	0.88	1.2	1.2	1.4	2.3	3.2
1,2,3,7,8-PeCDD	0.87	1.0	0.83	1.0	2.0	44
1,2,3,4,7,8-HxCDD	0.94	1.9	0.60	0.82	1.7	1.8
1,2,3,6,7,8-HxCDD	2.5	5.3	1.9	2.3	4.1	5.7
1,2,3,7,8,9-HxCDD	1.7	3.9	1.6	1.9	3.8	3.6
1,2,3,4,6,7,8-HpCDD	31	143	53	67	110	92
2,3,7,8-TCDF	6.6	8.1	6.6	7.7	12	43
1,2,3,7,8-PeCDF	22	11	8.8	10	16	0.58
2,3,4,7,8-PeCDF	9.3	8.8	6.6	8.2	14	14
1,2,3,4,7,8-HxCDF	26	14	10	11	19	19
1,2,3,6,7,8-HxCDF	10	7.6	5.0	6.7	13	11
1,2,3,7,8,9-HxCDF	3.9	1.7	1.6	2.4	2.9	3.4
2,3,4,6,7,8-HxCDF	6.9	8.8	8.2	9.9	18	22
1,2,3,4,6,7,8-HpCDF	16	39	31	36	70	55
1,2,3,4,7,8,9-HpCDF	3.5	2.5	2.0	2.6	2.7	5.3
TEQ excl. LOD	12	12	8.9	11	19	40
TEQ ½ LOD	12	12	8.9	11	19	40
TEQ incl. LOD	12	12	8.9	11	19	40

Table S 28 Congener and homologue specific concentrations of PCBs and PCDD/PCDFs in I2

I2	<2000 µm >1000µm	<1000 µm >500 µm	<500 µm >250µm	<250 µm >125µm	<125 µm >63 µm	< 63 µm
PCB homologues	**(µg//kg)**	**(µg//kg)**	**(µg//kg)**	**(µg//kg)**	**(µg//kg)**	**(µg//kg)**
TriPCBs	3752	5399	5488	6395	683	250
TetraPCBs	5134	5691	7518	9973	471	232
PentaPCBs	1606	1990	2460	3349	251	120
HexaPCBs	688	919	1233	1976	233	168
HeptaPCBs	198	286	434	700	63	38
OctaPCBs	24	35	48	96	3.1	
NonaPCBs	0.85	1.4	2.0	3.8		
DecaPCB	0.14	0.50	0.46	0.79	0.50	0.23
PCB congeners	(µg//kg)	(µg//kg)	(µg//kg)	(µg//kg)	(µg//kg)	(µg//kg)
PCB #28	586	782	1023	1153	83	28
PCB #52	434	494	617	801	66	26
PCB #101	229	287	354	492	52	32
PCB #153	120	162	210	339	33	27
PCB #138	156	223	295	462	33	31
PCB #180	54	81	115	202	14	8.8
PCB #81	5.8	8.1	12	16	17	18
PCB #77	35	48	71	92	108	117
PCB #126	0.74	1.1	0.92	1.7	2.6	2.9
PCB #169	0.018	0.028	0.57	0.56	0.067	0.070
PCB #123	8.0	9.9	12	18	1.5	0.82
PCB #118	176	240	278	405	18	9.3
PCB #114	6.7	9.5	12	15	0.45	0.35
PCB #105	89	130	163	221	4.3	5.2
PCB #167	6.6	9.0	13	20	1.1	1.4
PCB #156	15	21	30	48	4.5	1.3
PCB #157	2.8	4.5	5.6	8.1	1.0	0.34
PCB #189	1.3	1.9	1.9	4.8	0.43	3.0
TEQ excl. LOD	0.089	0.13	0.13	0.21	0.28	0.31
TEQ ½ LOD	0.089	0.13	0.13	0.21	0.28	0.31
TEQ incl. LOD	0.089	0.13	0.13	0.21	0.28	0.31
PCDD/PCDF homologues	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)
TCDD	3.8	6.0	17	27	28	33
PCDD	9.5	20	38	46	42	46
HxCDD	20	30	92	89	83	116
HpCDD	43	125	161	332	457	453
OCDD	155	409	559	1591	2235	2169
TCDF	59	129	208	293	396	389
PCDF	33	72	164	174	249	247
HxCDF	38	50	50	113	136	158
HpCDF	18	35	243	177	83	148
OCDF	19	35	86	112	177	192
PCDD/PCDF congeners	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)	(ng/kg)
2,3,7,8-TCDD	2.0	0.83	3.8	0.15	2.3	2.5
1,2,3,7,8-PeCDD	1.1	2.1	1.7	0.36	1.1	2.7
1,2,3,4,7,8-HxCDD	1.1	2.3	1.7	1.0	1.5	4.3
1,2,3,6,7,8-HxCDD	2.6	3.1	4.6	6.6	7.1	9.9
1,2,3,7,8,9-HxCDD	2.0	1.2	0.70	3.9	2.6	5.0
1,2,3,4,6,7,8-HpCDD	22	58	78	168	240	230
2,3,7,8-TCDF	6.9	13	16	18	33	31
1,2,3,7,8-PeCDF	2.6	4.4	9.4	11	17	15
2,3,4,7,8-PeCDF	4.2	7.1	11	17	29	25
1,2,3,4,7,8-HxCDF	3.9	4.7	9.5	12	20	23
1,2,3,6,7,8-HxCDF	1.8	2.5	2.9	4.6	8.3	7.3
1,2,3,7,8,9-HxCDF	0.92	0.42	1.5	0.29	2.9	4.2
2,3,4,6,7,8-HxCDF	8.7	6.0	4.1	6.8	11	13
1,2,3,4,6,7,8-HpCDF	7.1	14	33	48	61	78
1,2,3,4,7,8,9-HpCDF	2.1	1.1	1.3	0.86	8.7	8.5
TEQ excl. LOD	6.6	7.7	12	14	24	24
TEQ ½ LOD	6.6	7.7	12	14	24	24
TEQ incl. LOD	6.6	7.7	12	14	24	24

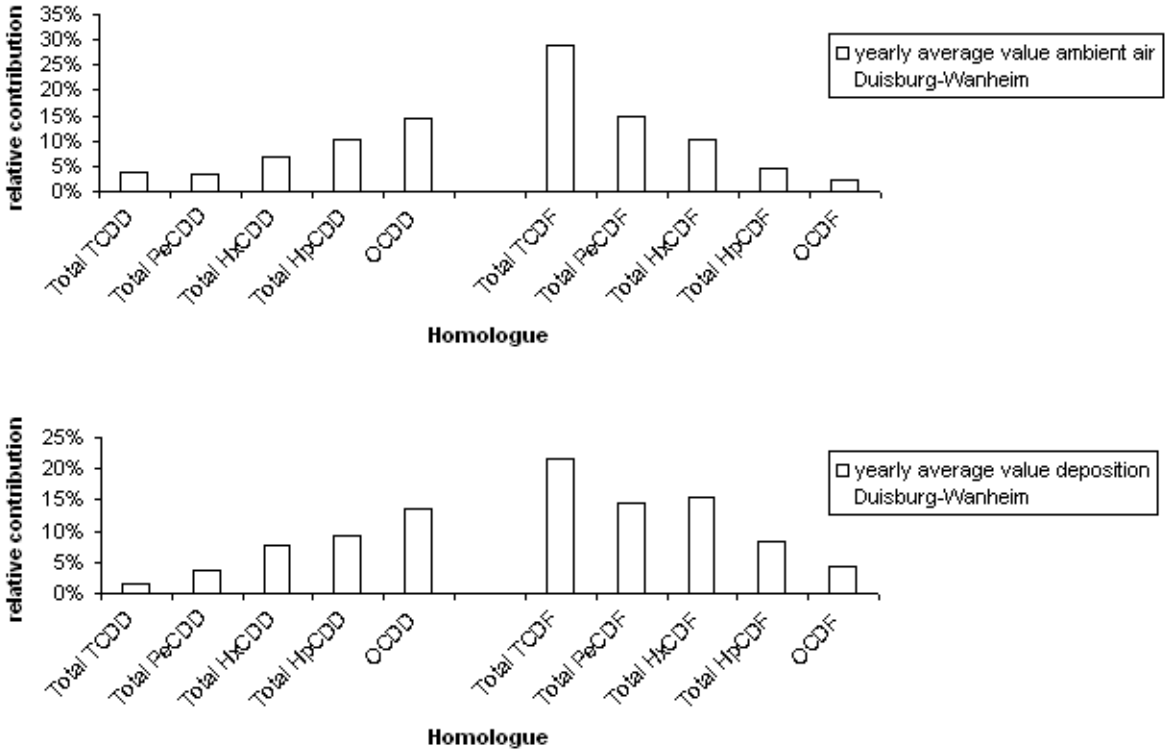


Figure S 25 Homologue distribution of PCDD/PCDF in ambient air (upper panel) and in deposition (lower panel) in Duisburg-Wanheim expressed as yearly average values. Homologue patterns are expressed as the relative contribution of each homologue to the sum of total PCDD/PCDF.

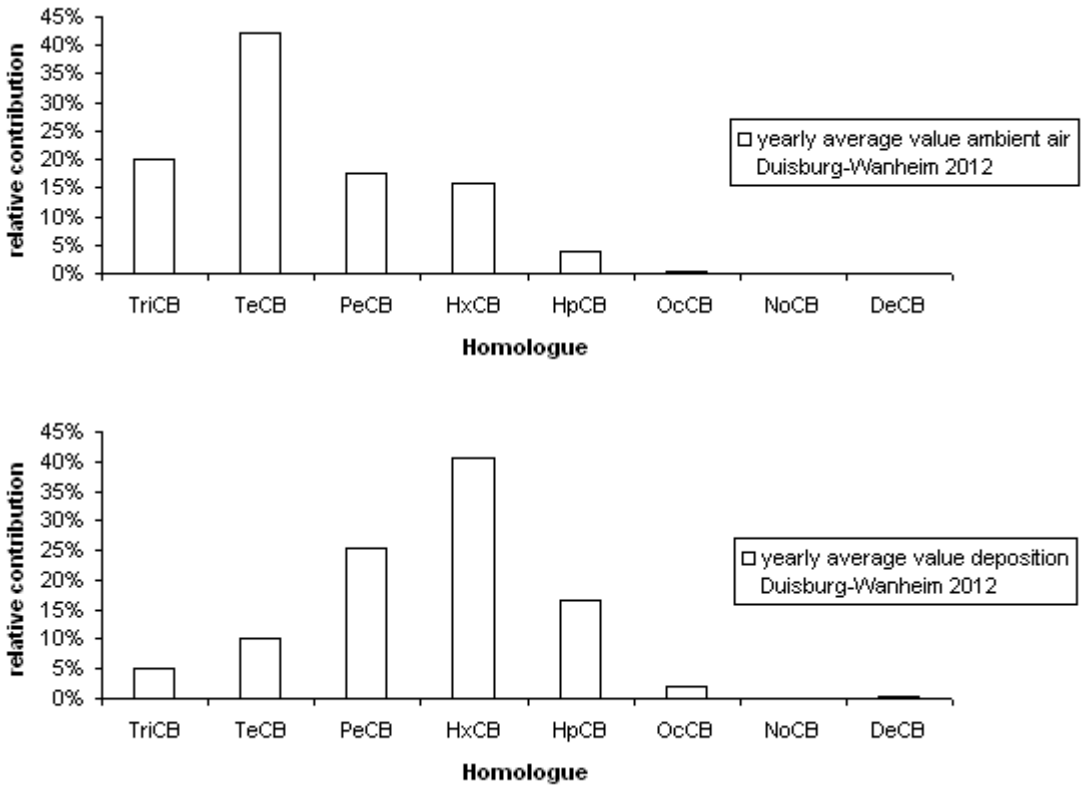


Figure S 26 Homologue distribution of PCB in ambient air (upper panel) and in deposition (lower panel) in Duisburg-Wanheim expressed as yearly average values. Homologue patterns are expressed as the relative contribution of each homologue to the sum of tri- to decachlorobiphenyls.

Table S 29 Concentrations of dl-PCB TEQs and PCDD/PCDF TEQs in soil samples from NRW. Samples were analyzed in 2011/2012. In addition contribution of individual TEQ to total TEQ (dl-PCB TEQ+ PCDD/PCDF TEQ) is shown.

Description	dl-PCB TEQ (ng/kg)	PCDD/PCDF TEQ (ng/kg)	% dl-PCB TEQ	% PCDD/PCDF TEQ
Hochsauerlandkreis	0.39	3.1	11%	89%
Hochsauerlandkreis	0.40	2.5	14%	86%
Hochsauerlandkreis	0.44	3.1	12%	88%
Hochsauerlandkreis	0.56	2.1	21%	79%
Städteregion Aachen	1.9	4.5	29%	71%
Städteregion Aachen	1.1	5.0	18%	82%
Paderborn	0.49	3.1	14%	86%
Paderborn	0.53	2.2	20%	80%
Köln	0.43	1.9	19%	81%
Rheinisch-Bergischer Kreis	1.2	6.1	16%	84%
Rheinisch-Bergischer Kreis	1.0	4.3	19%	81%
Rheinisch-Bergischer Kreis	0.51	1.9	21%	79%
Oberbergischer Kreis	0.48	2.5	16%	84%
Oberbergischer Kreis	0.63	2.3	22%	78%
Warendorf	1.2	4.3	22%	78%
Warendorf	0.27	1.4	16%	84%
Borken	0.26	1.3	17%	83%
Borken	0.32	1.5	17%	83%
Lippe	0.53	1.9	22%	78%
Lippe	0.39	2.0	17%	83%
Siegen-Wittgenstein	0.39	1.8	18%	82%
Siegen-Wittgenstein	0.79	4.9	14%	86%
Siegen-Wittgenstein	0.50	2.7	16%	84%
Siegen-Wittgenstein	0.48	2.3	17%	83%
Kleve	8.8	41	18%	82%
Kleve	1.1	6.5	15%	85%
Kleve	1.5	4.6	25%	75%
Kleve	0.40	2.7	13%	87%
Kleve	0.40	2.9	12%	88%
Wesel	0.60	2.5	19%	81%
Wesel	0.60	2.7	18%	82%
Wesel	1.5	6.8	18%	82%
Wesel	1.8	7.4	20%	80%
Wesel	0.80	3.7	18%	82%
Wesel	1.2	4.0	23%	77%
Wesel	1.4	5.6	20%	80%
Wesel	0.50	2.0	20%	80%
Wesel	1.6	6.2	20%	80%
Wesel	0.60	2.8	17%	83%
Wesel	0.60	2.5	19%	81%
Wesel	1.1	4.2	21%	79%

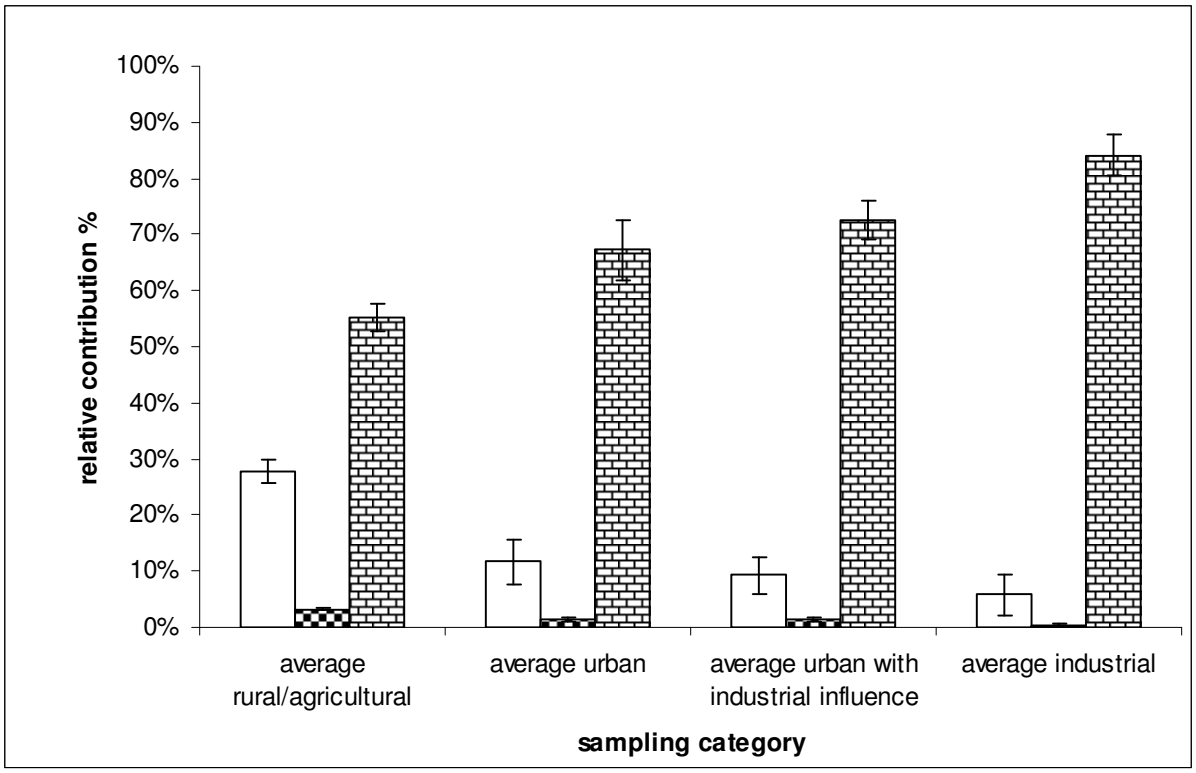


Figure S 27 Relative contribution of PCB #126 (blank), PCB #169 (checkerboard) and PCB #77 (masoned) to total non-ortho PCBs in street dusts with respect to source area. Standard deviation of the contribution in each individual sample are indicated as error bars.

Figure S 28 shows the mass fractions within individual particle size ranges of 16 street dust samples and two additional dust samples taken on industrial sites. The particle size/mass distribution does not follow any clear trend. For example, for U1 and sample UI7 no particles could be sampled for the largest particle-size fraction, only for sample 6 the highest mass fraction was present in the smallest particle size range. However, in general, the dominant particle sizes range from 500 to 125µm, which is reflected in the average median particle diameter of all samples (480 µm). Irvine et al. investigated the particle size distribution in 11 street dust samples of South Buffalo, NY (Irvine and Loganathan, 1998). They found median diameters from 180-870 µm. An average median diameter of 400 µm can be assumed for their study, which is rather close to the one found in this study.

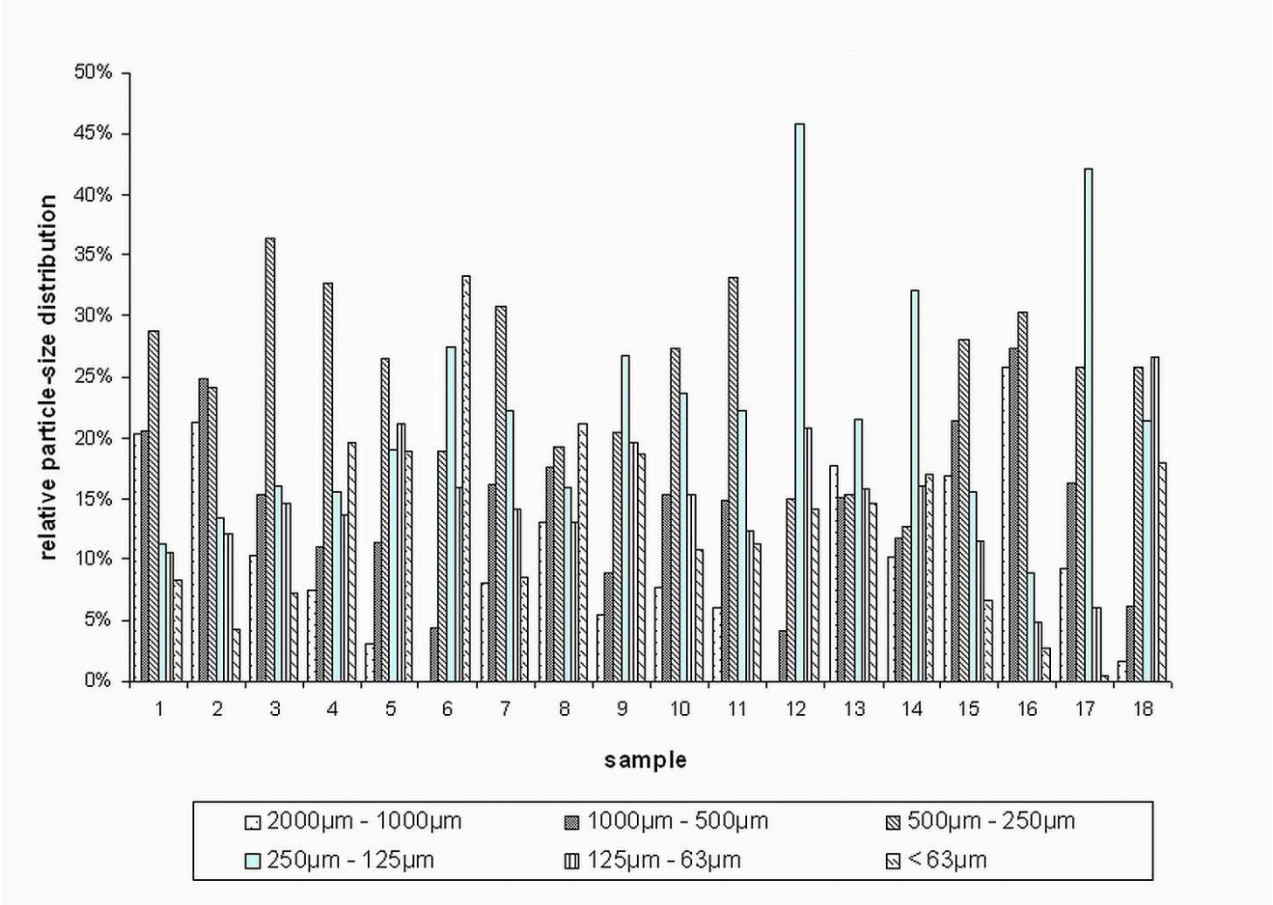


Figure S 28 Mass fractions of particle size classes of investigated street dust and industrial dust sample

Table S 30 PCB6, dl-PCB TEQ and PCDD/PCDF TEQ concentrations for individual particle size fractions are shown. In addition, mass fractions (% mf) of each particle size fraction are given.

Sample	> 1000 µm to < 2000 µm			> 500 µm to < 1000 µm			> 250 µm to < 500 µm			> 125 µm to < 250 µm			> 63 µm to < 125 µm			< 63 µm		
	PCB6 µg/kg	PCDD/PCDF TEQ ng/kg	dl-PCB TEQ ng/kg	PCB6 µg/kg	PCDD/PCDF TEQ ng/kg	dl-PCB TEQ ng/kg	PCB6 µg/kg	PCDD/PCDF TEQ ng/kg	dl-PCB TEQ ng/kg	PCB6 µg/kg	PCDD/PCDF TEQ ng/kg	dl-PCB TEQ ng/kg	PCB6 µg/kg	PCDD/PCDF TEQ ng/kg	dl-PCB TEQ ng/kg	PCB6 µg/kg	PCDD/PCDF TEQ ng/kg	dl-PCB TEQ ng/kg
UI1	-	1.0	-	-	0.83	-	-	1.0	0.90	-	3.5	2.5	50	10	6.8	39	13	8.9
% mf		20.4			20.6			28.8			11.3			10.6			8.3	
UI2	39	22	7.4	37	19	5.2	62	23	9.9	94	54	15	91	53	18	210	66	36
% mf		21.3			24.8			24.1			13.5			12.1			4.3	
UI3	-	2.4	1.7	-	2.0	4.5	-	2.3	3.6	35	8.4	6.5	78	21	14	140	30	25
% mf		10.3			15.3			36.4			16.1			14.6			7.3	
UI4	-	1.8	1.8	-	1.9	2.9	-	2.0	1.7	70	3.1	7.9	45	4.3	8.4	85	8.6	15
% mf		7.5			11.1			32.7			15.5			13.7			19.6	
UI5	-	2.9	2.5	-	1.8	1.9	-	1.6	2.3	-	2.0	3.8	-	2.3	6.3	110	4.3	16
% mf		3.0			11.5			26.6			19.0			21.1			18.8	
UI6	-		-	62	25	5.4	-	1.5	0.77	-	2.2	0.76	-	4.3	3.1	-	3.1	1.8
% mf		-			4.2			15.0			45.6			20.8			14.2	
UI7	-	9.4	5.9	-	5.8	6.4	74	10	8.8	45	48	14	57	29	14	69	44	17
% mf		17.7			15.1			15.3			21.3			15.9			14.6	
UI8	65	6.4	11	82	8.2	17	81	6.6	22	230	22	77	270	26	90	240	23	82
% mf		10.2			11.9			12.7			32.2			16.1			17.0	
U1	-		-	62	3.6	6.8	110	3.4	10	89	4.6	12	150	7.2	20	160	11	22
% mf		-			4.4			18.8			27.5			15.9			33.3	
U2	-	2.2	1.7	-	1.5	3.1	54	1.4	3.4	63	3.1	6.0	94	7.6	17	110	7.1	13
% mf		8.1			16.1			30.8			22.2			14.1			8.6	
U3	-	0.90	-	-	1.1	0.77	-	1.2	1.4	45	1.7	9.0	35	2.6	4.0	37	2.8	6.1
% mf		13.0			17.7			19.2			15.9			13.0			21.1	
U4	40	1.7	3.4	-	1.6	3.0	-	2.2	2.1	52	8.6	7.7	130	5.7	12	190	7.8	9.4
% mf		5.4			8.9			20.5			26.8			19.6			18.8	
U5	-	0.64	0.77	-	0.68	-	-	1.0	1.6	-	2.5	2.8	65	3.0	8.7	95	4.7	12
% mf		7.6			15.3			27.4			23.6			15.3			10.8	
U6	32	2.7	4.9	290	5.2	19	66	4.3	8.5	190	5.6	14	200	11	24	190	12	24
% mf		6.0			14.8			33.2			22.2			12.4			11.3	
R1	-	0.89	1.7	-	0.92	1.9	-	1.9	5.1	110	4.3	21	64	4.8	16	48	6.4	15
% mf		16.9			21.3			28.0			15.6			11.6			6.7	
R2	-	1.4	1.9	-	2.3	2.6	-	2.1	3.9	59	3.0	13	34	3.8	14	37	6.7	15
% mf		25.8			27.4			30.2			8.9			4.8			2.8	
I1	170	12	45	540	12	49	870	9	118	170	11	64	740	19	83	570	40	60
% mf		9.3			16.3			25.7			42.1			6.0			0.48	
I2	1600	6.6	89	2000	7.7	129	2600	12	127	3400		218	280	24	282	150	24	307
% mf		1.6			6.1			25.9			6.1			26.8			18.0	

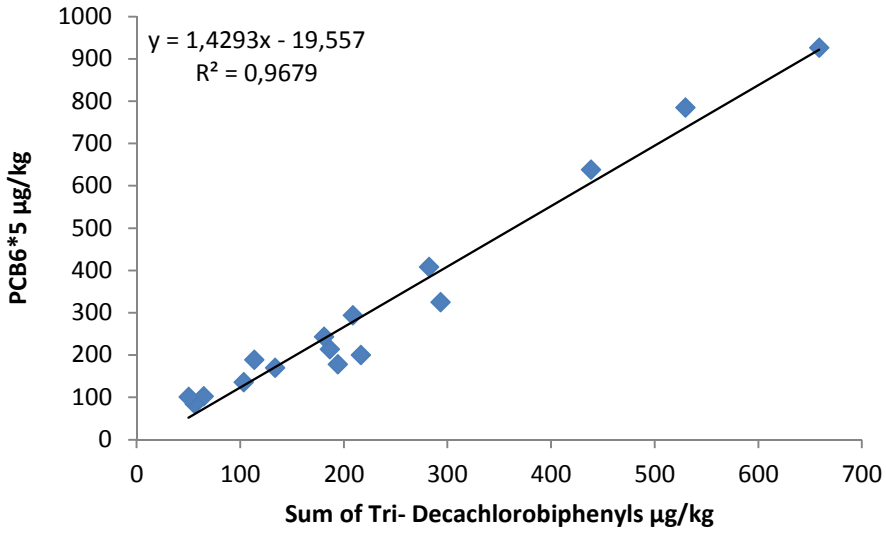


Figure S 29 Correlation of the sum of tri- to decachlorobiphenyls and PCB6*5 in street dust samples. Furthermore the linear regression function and the correlation coefficient are depicted.

Reference

Irvine, K.N.; Loganathan, B.G. Localized enrichment of PCB levels in street dust due to redistribution by wind. Water. Air and Soil Pollution 1998, 105, 603–615.

4. Analysis of polychlorinated biphenyls, polychlorinated dibenzo-p-dioxins and dibenzofurans in particulate and oily films on impervious surfaces

Submitted to *Science of the Total Environment* as "Klees, M.; Hiester, E.; Schmidt, T.C. Analysis of polychlorinated biphenyls, polychlorinated dibenzo-p-dioxins and dibenzofurans in particulate and oily films on impervious surfaces."

4.1 Introduction

Polychlorinated biphenyls (PCBs) as well as polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/PCDF) are persistent organic pollutants (POPs), which are known for their toxicity and widespread distribution in the environment. Metallurgic plants, combustion processes like municipal waste incineration or accidental fires are known as significant primary PCDD/PCDF emission sources, whereas PCBs were man-made formulations used in large scale, e.g., in transformers, in condensers or in open applications such as in paints, sealing materials or as additives in plastics. The global production of PCBs was estimated to 1.3 million tons [Breivik et al., 2002]. For Germany it was estimated that 24'000 tons of PCBs were used in open application since the production started in 1929, and 59'000 tons of PCBs were estimated to be produced for closed applications (transformer, condenser) [Bruckmann et al., 2013]. Since emission of PCDD/PCDFs and PCBs has been comprehensively regulated, long term monitoring programs showed significant decreases in pollution, especially for PCDD/PCDFs [Bruckmann et al., 2013]. Secondary contamination such as the diffuse release of contaminated materials during recycling processes or the remobilization from sinks such as soils and dusts have been found to play a major role in the fate of persistent organic pollutants and to slow down or even to level the decrease of PCDD/PCDFs and PCBs in ambient air and atmospheric depositions [Bruckmann et al., 2013; Klees et al., 2015]. Improper handling of PCB contaminated transformer by a recycling enterprise resident in the harbour area of Dortmund and the identification of secondary PCB emission originating from the aforesaid enterprise [Bruckmann et al., 2011], initiated a systematic survey of industrial facilities, in particular waste management facilities, dealing

with potentially PCB or PCDD/PCDF contaminated materials in North Rhine-Westphalia (NRW). During the individual inspections of those industrial facilities wipe samples were among other sample matrices taken in order to assess the contamination situation. Samples were taken from the working areas as well as from staff rooms of those investigated industrial facilities. PCB and PCDD/PCDF area concentrations in wipe samples were evaluated in comparison with a remediation target that was previously established for the cleaning of surfaces from indoor environments after a fire event [Gesamtverband der Deutschen Versicherungswirtschaft, 2007]. Wipe sampling seems to be a suitable sampling technique for the determination of hazardous contaminants in films developed or deposited on impervious surfaces. This has been successfully demonstrated in various measurement programs related to environmental, occupational hygiene or monitoring issues [Butt et al., 2004; Stapleton et al., 2008; Stout et al., 2009; Toms et al., 2009]. Wipe sampling is relatively inexpensive, requires little maintenance and its handling is quite easy. An overview of applications for wipe sampling and used methods depending on the contaminants of concern emphasized that surface roughness and the use of validated wipe materials and wetting agents are of major importance for sampling specifications like reproducibility or transfer efficiencies [Billets, 2007]. Diverse wipe materials including filter papers, cotton gauze pads, glass wool, cotton wool plugs, cotton cloth wipes, Kimwipes or even Kleenex® were used in recent years as wipe material for the collection of PCBs or PCDD/PCDFs from impervious surfaces [Ruokojärvi et al., 2000; Lioy et al., 2002; Butt et al., 2004; Billets, 2007]. However, cotton wiping materials, namely cotton wipes or cotton gauze, were found to be the preferred material since cotton wipes are commercially available and differ from other materials through high mechanical robustness and hence are from a practical point of view beneficial [Deziel et al., 2011; EPA/600/R-08/079, 2008; Bernard et al., 2008]. Furthermore, the elimination of possible blank values in a pre-cleaning step is essential for all wipe materials. If wetting agents were applied, isooctane, n-hexane, octane, methanol, 2-propanol, toluene or water was used for the collection of PCBs and PCDD/PCDFs [Ruokojärvi et al., 2000; Butt et al., 2004; Billets, 2007]. Information about the transfer efficiencies of PCBs and PCDD/PCDFs during wipe sampling are not available in the current literature. In order to enable a quantitative determination of surface contaminations, knowledge of transfer efficiencies during sampling is essential and has to be investigated as it has been successfully demonstrated, e.g., for the determination of PCBs and PCDD/PCDFs in street dust samples or for pesticides in wipe samples taken on impervious surfaces [Bernard et al., 2008; Deziel et al., 2011; Klees et al., 2013]. Glass surfaces are representative for impervious surfaces

characterized by a smooth surface, including also metal surfaces or ceramic tiles. Since it was proposed that semivolatile organic compounds (SOCs) partition into developing films on impervious surfaces [Law and Diamond, 1998], glass surfaces or rather window surfaces appear to be preferably chosen as sampling surface as reported in previous studies [Diamond et al., 2000; Butt et al., 2004].

Therefore, the first goal of the present study is to examine wipe sampling transfer efficiencies of individual low concentrated PCB and PCDD/PCDF congeners in particulate films (PFs) and oily liquid films (OFs) from an impervious glass surface to a wipe sample. Transfer efficiencies were investigated with regard to the state of matter and to the wetting solvents applied to the cotton wipe used for sampling. Transfer efficiencies of OFs were determined after wiping with n-hexane, n-heptane and toluene, whereas transfer efficiencies of PCBs and PCDD/PCDFs in PFs were examined with n-hexane as wetting agent. In addition, the application of pressurized liquid extraction (PLE) in the analysis schemes of PCBs and PCDD/PCDFs in wipe samples was tested. To our knowledge this is the first study that uses PLE for the simultaneous extraction of PCBs and PCDD/PCDFs from wipe samples. Due to the different types of wiping materials and wetting agents reported in the literature for the collection of films on impervious surfaces containing PCBs and/or PCDD/PCDFs, we introduce a wipe sampling monitoring method simultaneous determination of PCB and PCDD/PCDF area concentrations on impervious surfaces. The feasibility of the analytical method was checked for various types of wipe samples by calculating the relative percentage of quantifiable individual congener concentrations that exceeded the sampling area specific limit of detection (LOD). Finally, area concentration data for PCBs and PCDD/PCDFs in wipe samples were measured and differences in concentration levels of PCBs correlated to the industrial sector.

4.2 Materials and method

4.2.1 Chemicals and materials

Toluene, n-hexane, n-heptane and dichloromethane used during transfer efficiency experiments, extraction and clean-up for PCB and PCDD/PCDF analysis were all of picograde quality, purchased from LGC Promochem (Wesel, Germany). H_2SO_4, NaOH and $AgNO_3$ used during the clean-up were acquired from Merck (Darmstadt, Germany) and were of analysis quality. Alumina used for the chromatographic separation of PCBs and PCDD/PCDFs was purchased from MP Biomedical (MPAlumina B – Super I, MP

Biomedicals, Eschwege, Germany). The $^{13}C_{12}$-PCB and PCDD/F standards for isotope dilution analysis were delivered by Cambridge Isotopes Laboratories (Andover, USA). For transfer efficiency experiments of PCBs and accuracy check of the analytical method, BAM CRM 5001 (BAM Federal Institute for Materials Research and Testing, Berlin, Germany) was used and for transfer efficiency experiments of PCDD/PCDFs a commercially available mixture of native PCDD/PCDFs (NK-ST-B2, Campro Scientific GmbH, Berlin, Germany), respectively.

4.2.2 Wipe pre-cleaning

The cotton cloth wipes (225 mm x 225 mm Fa. Plano, Wetzlar, Germany) were pre-cleaned to eliminate contamination with PCBs and PCDD/PCDFs or other chemical interferences originating from the manufacturing process, which could disturb the analytical determination. To that end, a bulk of approx. 20 wipes was extracted via Soxhlet in 3 L toluene for at least 24 h. Subsequently, further pre-cleaning of single wipes was performed via Soxhlet in 300 mL toluene for another 24 h. After extraction a pre-cleaned single wipe was folded twice and enveloped in alumina foil for drying and storage in a laboratory oven at 50°C until usage.

4.2.3 Wipe sampling

Prior to wipe sampling of PFs or OFs the cotton cloth wipe was wetted with n-hexane (PF and OF), n-heptane (OF) or toluene (OF). Before sampling was started, (1) the wipe was folded twice in half and a portion of 10 mL wetting solvent was used to saturate the sample side without spill of wetting agent droplets. Wiping was started in the first direction from left-to-right and was finished in the second direction from up-to-down. Generally, one wiping procedure is defined as the total sampling area was wiped in vertical and horizontal direction (see Figure S2). (2) During a wiping procedure, the wipe was unfolded once and the sample side was turned inward to continue sampling. If necessary, rewetting of the sample side with 10 mL wetting solvent was performed. Further the wipe was unfolded and sampling step (1) and (2) were repeated with the inward of the wipe for the completion of the wiping procedure. After sample collection the wipe was placed in a pre-cleaned 100 mL screw cap bottle (Schott, Mainz, Germany) and stored at max. +6 °C until extraction. An illustration of the wiping scheme can be seen in the Supporting Information.

4.2.4 Application to real wipe samples

Before wiping of real samples was started the designated sampling area was marked and the actual sampling area was documented. A criterion that all surfaces have to fulfil is that they

have to be to the greatest extent smooth and impervious. Glass surfaces or metal surfaces are suitable for sampling. During the inspections of industrial facilities wipe samples were taken from working areas as well as from surfaces of social areas. For the evaluation of PCDD/PCDFs immission sampling sites downwind the fire accidents were chosen and samples were taken randomly from surfaces that visually exhibited particle loads that could be likely ascribed to the fire event. During those fires windscreens of cars parking next to the fire event were preferred to be investigated by wipe sampling.

During this study PCB6 (the sum of the six indicator PCBs #28, #52, #101, #138, #153, #180) and dl-PCB (PCB #105, #114, #118, #123, # 156, #157, #167, #189) TEQ (toxicity equivalent) concentrations were analysed in 61 wipe samples. Therefrom 51 wipe samples were analysed during the inspections of working areas and social rooms of waste management facilities and 6 samples were analysed originating from resident houses. Furthermore, 4 samples were taken from exterior window surfaces (WS). From four different sectors of waste management wipe samples were taken. To be specific, 6 six samples were taken from the waste oil management sector, 6 samples were taken from metal recycling sector, 16 sample were taken from the electronic scrap recycling sector, 9 samples were taken from the transformer recycling management. Additional 9 samples were taken in temporary deposits for hazardous waste and 4 samples were taken from surfaces of hazardous waste incineration plants. For one sample no suitable classification was possible. PCDD/PCDF TEQ concentrations were determined in 6 resident house surface wipes and in 4 samples from exterior window surfaces. In cases of accidental major fires 13 wipe samples were taken for the evaluation of the input of PCDD/PCDFs originating from those fires to terrestrial or aquatic systems. An overview of all investigated samples and PCB6, dl-PCB TEQ and PCDD/PCDF TEQ concentrations is presented in the Supporting Information. An overview of PCB6 and dl-PCB TEQ concentrations with respect to the sector of waste management and PCDD/PCDF TEQ in wipe samples related to accidental heavy fires can be seen in **Table 12**.

4.2.5 Extraction, clean-up and analysis

The analysis scheme for the determination of PCBs and PCDD/PCDFs in wipe samples is depicted in **Figure 14.** Extractions of wipe samples examined during method validation were performed with PLE using a Dionex ASE 200 system (Sunnyvale, USA). A previously developed and standardized PLE method for the simultaneous extraction of PCBs and PCDD/PCDFs from street dust samples [Klees et al., 2013] was adopted, slightly modified and applied for wipe sample extraction. To fully utilize the 33-mL PLE cell volume, the wipe has to be folded twice and rolled up as can be seen in **Figure S 30**.

Samples taken from staff rooms and working areas of facilities dealing in day-to-day business with PCB containing materials and wipe samples collected after heavy accidental fires were extracted via Soxhlet as described previously by the authors [Klees et al., 2013]. Deviating from the described Soxhlet extraction method, extraction was performed without a glass fibre thimble. After extraction the crude sample extracts were subjected to the clean-up and fractionation process as described elsewhere [Klees et al., 2013], but an additional fractionation step was introduced for the wipe as described in the following (**Figure 14**). The PCB fraction was subjected to a second alumina column to separate indicator (PCB #28, #52, #101, #138, #153, #180) and mono-ortho PCBs (PCB #105, #114, #118, #123, # 156, #157, #167, #189) from non-ortho PCBs (#77, #81, #126, #169). The alumina column was pre-washed with 70 mL n-hexane and the PCB fraction solved in approx. 2 mL toluene was applied to the column. The first fraction containing indicator and mono-ortho PCBs was eluted using 150 mL 96:4 (v/v) n-hexane/dichloromethane mixture, whereas non-ortho PCBs were eluted in a second fraction using 100 mL 90:10 (v/v) n-hexane/dichloromethane [Loos et al., 2007]. Concentration of both PCB eluates was performed via nitrogen flow to 100 µL in n-decane [Klees et al., 2013]. However for some determinations the final volume and the injection volume had to be adjusted. This has been performed if due to high oil content of the wipe sampled matrix peak broadening of especially lower chlorinated PCBs during the first chromatography run had been observed. Then the final volume was elevated to approx. 300 µL and injection volume differed between 0.3 and 1.0 µL for a second run. Furthermore, indicator and mono-ortho PCBs and homologue groups (tri- to decachlorobiphenyl) were determined with high resolution mass spectrometry using mass spectrometric conditions and the gas chromatograph oven temperature program as described by the authors [Klees et al., 2013]. Additional information on recorded qualification and quantification mass-to-charge can be taken from **Table S 32** and **Table S 33**.

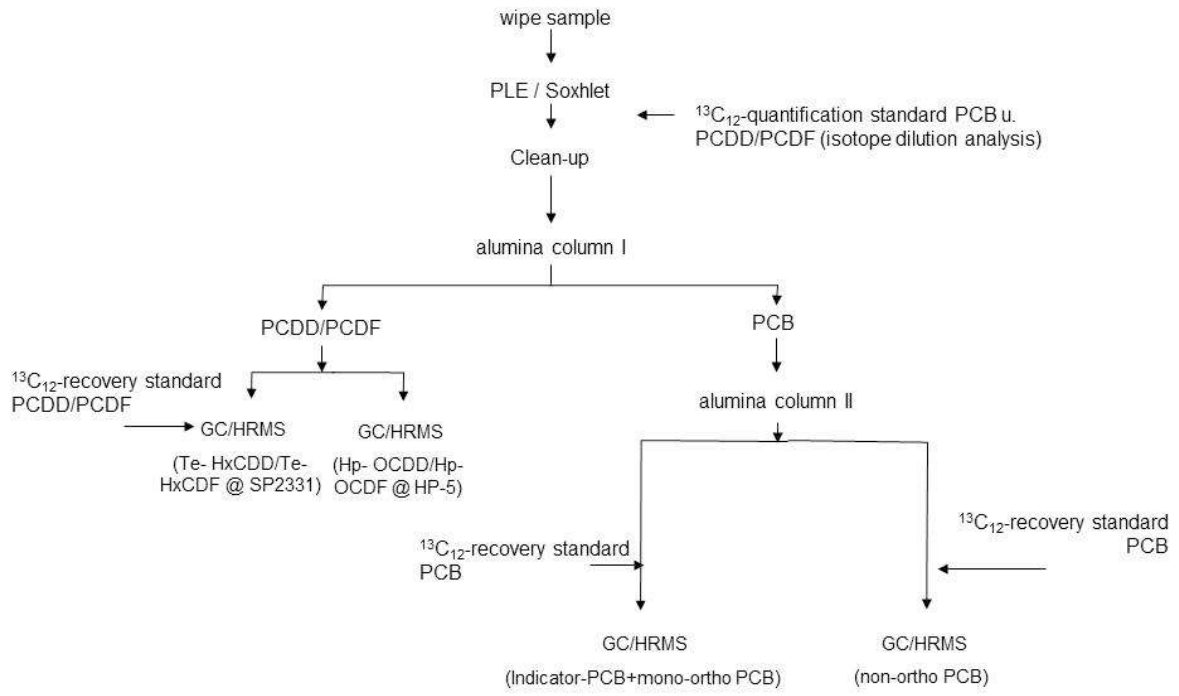


Figure 14 Analysis scheme for the determination of PCBs and PCDD/PCDFs in wipe samples. GC columns used for PCDD/PCDF analysis are indicated (SP2331 = polar; HP-5 = non-polar).

In contrast to the analysis of all 2,3,7,8 chlorine substituted PCDD/PCDFs and homologue groups described before [Klees et al., 2013], hepta- and octachlorinated PCDD/PCDFs congeners and homologues were analysed using a HP-5 column (J&W) (50 m; 0.20 mm I.D.; 0.11 µm film thickness). To that end, the gas chromatograph oven temperature program was started at 100 °C and held for 1.50 min, heated to 180 °C at a rate of 20 °C min^{-1}, and then heated to the final temperature of 300 °C at a rate of 10 °C min^{-1}, which was held for 5 min. Additional information to recorded qualification and quantification mass-to-charge ratios m/z can be taken from **Table S 31**.

4.2.6 Transfer of PCBs and PCDD/PCDFs during wipe sampling

In order to produce a surrogate for PFs containing low concentrations of PCBs and PCDD/PCDFs, street dusts sampled from different sites of NRW were used. The particle fractions <2000 µm of each street dust sample were ground to <63 µm, combined and homogenized thoroughly. Concentrations of individual PCB and PCDD/PCDFs congeners

were determined using PLE combined to GC/HRMS method [Klees et al., 2013]. Determined concentrations for individual PCB and PCDD/PCDF congeners and homologues for PFs surrogate can be taken from the Supporting Information.

OFs were simulated by preparing a spiking solution composed of 50 µL BAM CRM 5001 transformer oil containing certified PCB concentrations and 50 µL of a mixture of native PCDD/PCDFs dissolved in toluene. The mixed spike solution was dissolved in 5 mL n-hexane for the investigations of the transfer of OFs. Previously, the density of BAM CRM 5001 was gravimetrically (n=10) determined to calculate the spiked masses of individual PCB congeners contained in 50 µL volume transformer oil (Table S6). An overview of the validation scheme can be seen in **Figure 15**.

Spiking of PFs was performed by suspending 1 g surrogate in approx. 5 mL n-hexane in a beaker, followed by quantitative dropwise transfer via Pasteur pipette onto the testing surface. To ensure quantitative spiking the beaker and the Pasteur pipette were rinsed thoroughly with n-hexane onto the surface. For the investigation of PCBs and PCDD/PCDFs transfer efficiencies during wipe sampling an impervious glass plate (area: 100 cm x 100 cm) mounted on plywood served as testing surface.

Similar to PFs, the spiking solution for OFs was quantitatively applied dropwise to the testing surface via Pasteur pipette. Rinsing of volumetric flask and Pasteur pipette was performed as already described. Concentration levels of individual PCB and PCDD/PCDFs congeners in the OFs spiking solution can be taken from the Supporting Information.

During the transfer experiments for PFs one wiping procedure was used, for OFs, four individual wiping procedures were sampled. For each wiping procedure an unused and pre-cleaned wipe was used. Prior to the application of spiking material the wipe surface was thoroughly cleaned with commonly used n-hexane wetted cellulose wipes. Application of the spike solution was not performed until the cleaned surface was air dried. After the application of the spike solution collection of the wipe samples was not performed until the remaining solvent was allowed to completely volatilize (10-15 min).

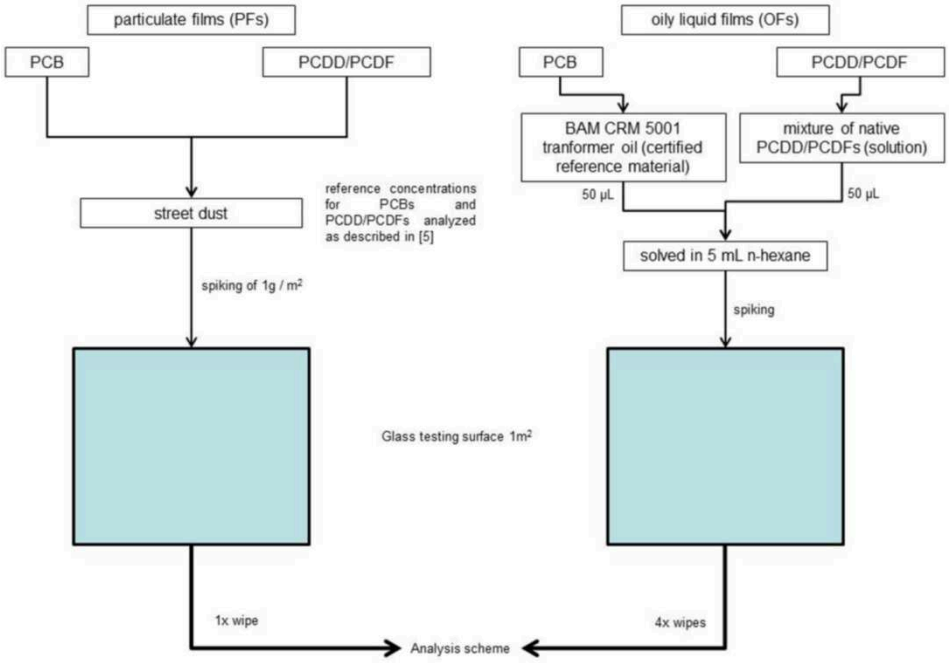


Figure 15 Validation scheme for transfer efficiency experiments of PFs and OFs.

4.2.7 Quality assurance

In addition to the quality assurance reported elsewhere [Klees et al., 2013], method blank value concentrations for each individual PCB and PCDD/PCDFs congener and homologue were checked during transfer experiments. The limit of detection (LOD) was defined as the average method blank value concentration for each PCB congener or homologue plus three times its standard deviation and limit of quantification (LOQ) was defined as average method blank value concentration for each PCB congener or homologue plus nine times its standard deviation. For PCDD/PCDF congeners detected during method blank analysis LOD was defined as the average method blank value concentration plus three times its standard deviation. For PCBs almost all congeners were at least once detected during method blank analysis and were considerably differing from analysis to analysis which requires to handle quantification criteria for PCBs more stringent as compared to PCDD/PCDFs. Alternatively, for congeners not detected during single method blank analyses LOD was established to be three times the baseline noise, which was determined during the analytical run of each sample extract individually. Furthermore, to assess information on the method performance, recoveries of $^{13}C_{12}$-PCB and PCDD/PCDFs quantification standards were monitored. Precision and accuracy were checked by spiking 50 µL of the testing standards (BAM CRM 5001 and the mixture of native PCDD/PCDFs) used during transfer efficiencies of OFs to the

cloth wipe and subsequently analysing in quadruplicate as described here. Analysed concentrations during this experiment were calculated on the area of the testing surface of 1 m^2.

4.2.8 Data analysis

The area concentration data for each single PCB congener or homologue were compared with the congener and homologue specific area dependent LOQ and area concentration data for each single PCDD/PCDF congener or homologue were compared with the congener and homologue specific area dependent LOD. Actual LOQ for single PCB or LOD for single PCDD/PCDF congeners or homologues can be taken **Table S 45**. Congeners that were below the LOD or LOQ were taken with half of the area dependent LOD or LOQ for the calculation of summary statistics like PCB6*5. PCB6*5 which is defined as the sum of the six indicator PCB (PCB #28, #52, #101, #138, #152, #180) times five according to EN 12766 is often used for the estimation of total PCB concentration [Petroleum products and used oils, 2001]. However, as it has been shown for street dust samples an overestimation of total PCB can occur if this convention is applied for the calculation of total PCB [Klees et al. 2015]. During the systematic survey of industrial facilities the action value of << 100 µg PCB6*5 / m^2 was adopted [Gesamtverband der Deutschen Versicherungswirtschaft, 2007; Schwerpunktinspektionsprogramm PCB, 2012]. In addition, for the evaluation of the cleaning effectiveness after PCB spill the PCB6*5 approach is successfully applied elsewhere [Verification of PCB spill cleanup by sampling and analysis, 1985]. Similar to the calculation of PCB6*5 area concentrations, congeners below the LOQ were taken with half of this value to account for the calculation of dioxin-like PCB toxicity equivalents (dl-PCB TEQs) or PCDD/PCDF TEQs.

After log-transformation of concentration data the Shapiro-Wilk test was performed to the data sets for the check of normality.

T-tests were used to check differences in concentration levels between social rooms and working areas on the one hand and the diverse sectors of waste management on the other hand, and for the comparison of transfer efficiencies using different wetting agents for wipe sampling. All statistical computations were performed with R 3.1.0 (R, 2013).

During the transfer efficiency experiments the expanded uncertainties were expressed as 95% confidence interval taken from the quadruplicate determinations of each analysed PCB and

PCDD/PCDF congener were used for the comparison with the confidence intervals analysed during spiking material validation.

4.3 Results and Discussion

4.3.1 Blank values, LODs and the approximation of the lower limit of wipe sample areas

Blanks have been observed for all PCB congeners in at least one single analysis. PCB method blanks of up to 4.0 ng / sample (PCB #138) were detected. Method blanks (n=10) could only be observed for the PCDD/PCDF congeners: 1,2,3,4,6,7,8-HpCDD, OCDD, 1,2,3,4,6,7,8-HpCDF, 1,2,3,4,7,8,9-HpCDF and OCDF. LOQs of individual PCB congeners were ranging from 0.013 ng / sample (PCB #126) to 16 ng / sample (PCB #153). LODs for the PCDD/PCDF congeners detected in at least one single blank value analysis were ranging from 0.75 pg / sample (1,2,3,4,7,8,9-HpCDF) to 41 pg / sample (OCDD). Surface films in outdoor and indoor environments are affected by gaseous, wet and particulate depositions on impervious surfaces and were evidently shown to accumulate SOCs, like PCBs or even PCDD/PCDFs, respectively [Eitzer and Hites, 1989; Law and Diamond, 1998; Diamond et al., 2000; Klees et al., 2015]. Therefore we approximated the lower limit of real wipe sampling areas in order to monitor comparative values for PCB area concentrations and for the determination of background area concentrations that develop on impervious outdoor surfaces. Those comparative values are based on the indicator PCBs or PCB6*5, respectively, which are of major importance in the Guidance on the Global Monitoring Plan for Persistent Organic Pollutants [UNEP, 2007]. In order to monitor the action value of << 100 µg PCB6*5/ m^2, it is not advisable to sample areas less than 0.0030 m^2 if the method introduced here is applied. Those approximated sampling areas correspond to sampling templates recommended by US EPA for the monitoring of effectiveness of cleaning after PCB spills [Verification of PCB spill cleanup by sampling and analysis, 1985]. For the approximation of the lower limit of wipe sampling areas taken from outdoor surfaces average yearly PCB congener specific concentrations in atmospheric depositions monitored in NRW in 2011(see **Table S 44**) total masses of collected materials on impervious surfaces (n=6; 0.16±0.14g) [Diamond et al., 2000] and yearly average total suspended atmospheric depositions (TSPD) from NRW (n=150; 0.17±0.086g/m^2*d) in 2011 were used [LANUV, 2014]. Literature data of wiped total masses compared to the average TSPD from NRW show similar mass loads to a daily

deposition load. From the simple equalizing of the congener specific LOD and the average yearly PCB congener specific concentration in atmospheric depositions the approximation of sampling areas can be performed. Owing to the calculations, we anticipate sampling areas of approx. 3 m^2. A calculation scheme can be exemplarily taken from the Supporting Information. Due to the use of atmospheric deposition data for the calculation of sampling areas of outdoor surfaces that can vary year by year this approach should be just regarded as an orientation value.

4.3.2 Pressurized liquid extraction of PCBs and PCDD/PCDFs from wipe samples

Recoveries of $^{13}C_{12}$-PCB- and $^{13}C_{12}$-PCDD/PCDF quantification standards were monitored in order to test the method performance of PLE of PCBs and PCDD/PCDFs collected with wipe samples. All sample extracts were subjected to the clean-up procedure described here. $^{13}C_{12}$-PCB quantification standards recoveries were ranging from 51% ($^{13}C_{12}$-DecaCB) to 70% ($^{13}C_{12}$- 2,3,3',4,4',5-HexaCB) with an average standard deviation (n=46) calculated for all congeners of 17%. Recoveries of $^{13}C_{12}$- PCDD/PCDF quantification standards were ranging after PLE between 60% ($^{13}C_{12}$-2,3,4,6,7,8-HxCDF) and 70% ($^{13}C_{12}$ – OCDF) with an average standard deviation (n=36) for all congeners of 12%. Recoveries of $^{13}C_{12}$-surrogate standards applied to street dust after PLE observed in a previous study (PCB: 41-78%; PCDD/PCDF: 70-87%) with those established in this study were comparable [Klees et al., 2015]. Studies dealing with the determination of PCBs and PCDD/PCDFs in wipe samples are mostly based on Soxhlet extraction methods in combination with gas chromatography coupled to electron capture detection [Diamond et al., 2000; Gingrich et al., 2001; Butt et al., 2004; Wu et al., 2008]. Even if mass spectrometry combined with isotope dilution analysis was used for detection, no data on recoveries of $^{13}C_{12}$-quantification standards as indicator for the extraction efficiency have been published previously [Wobst et al., 1999; Ruokojärvi et al., 2000]. A comparison of $^{13}C_{12}$-quantification standards recoveries after PLE of wipe samples with previous reports thus cannot be performed. However, within our own study, we used both Soxhlet and PLE and determined recoveries with both approaches (see

Table 10). As a result, ratios (PLE vs. Soxhlet) of congener specific $^{13}C_{12}$-quantification standard recoveries were calculated to 88-132%. Thus, it seems that PLE provides at least equivalent but especially for higher chlorinated congeners even increased recoveries for the indicator and mono-ortho PCB congeners in comparison with classical Soxhlet extraction.

Data of recoveries in all individual samples can be taken from the Supporting Information (**Table S 38** - **Table S 43**).

Table 10 Average percentage recovery rates and standard deviation of $^{13}C_{12}$–PCB quantification standards after PLE and Soxhlet extraction. In addition the ratios for the individual $^{13}C_{12}$–PCB quantification standards of PLE as compared to Soxhlet are depicted.

	PLE (%)	Soxhlet (%)	PLE vs. Soxhlet (%)[a]
	n=46	n=51	
PCB #28	67±24	69±25	96
PCB #52	65±19	68±23	96
PCB #101	65±15	67±23	97
PCB #123	65±16	72±25	90
PCB #118	65±17	69±23	94
PCB #114	68±15	74±25	92
PCB #105	65±13	73±24	88
PCB #153	66±11	70±25	94
PCB #138	68±11	71±25	96
PCB #167	63±11	65±23	97
PCB #156	68±13	67±25	101
PCB #157	70±14	66±23	107
PCB #180	63±10	57±21	111
PCB #189	67±14	55±21	121
PCB #194	63±10	52±21	122
PCB #208	60±10	52±21	115
PCB #209	51±13	39±18	132

[a] ratio of PLE as compared to Soxhlet $^{13}C_{12}$-recoveries

4.3.3 Determination of PCB and PCDD/PCDF in wipe samples

Evaluation of accuracy and reproducibility for individual PCB congeners was based on a certified reference material BAM CRM 5001. Five indicator PCBs #52, #101, #138, #153, #180 and in addition one mono-ortho PCB #118 were used for the comparison of experimentally determined concentrations with certified ones. The results are shown in **Figure 16**. Congeners that were not certified in BAM CRM 5001 were added to **Table S 36**. Furthermore, certified and non-certified PCB congener concentrations were converted into area concentrations. For evaluation of accuracy and reproducibility for the determination of PCDD/PCDFs in wipe samples, concentrations of individual 2,3,7,8 chlorine substituted PCDD/PCDF congeners in the testing standard used during transfer efficiency experiment of OFs were regarded as reference concentrations and were compared to the determined concentrations analysed during this spiking experiment.

The determination of individual PCBs in the wipe sample spiked with BAM CRM 5001 was performed in quadruplicate. After extraction via PLE the clean-up steps mentioned here were

applied to the extracts. A comparison of the certified and determined concentrations is shown in **Figure 16**. With the exception of PCB #138, the remaining indicator PCBs and the mono-ortho PCB #118 are within the confidence intervals provided by BAM. The possible co-elution of PCB #138 with other hexachlorinated congeners on a 5%-(phenyl)-polydimethylsiloxan stationary phase in combination with the comparatively high average blank value determined for PCB #138 may have caused the overestimation during accuracy analyses [Frame, 1997; BAM, 1998]. Regarding congener specific comparison of spiked PCDD/PCDF concentrations to determined concentrations the accuracy for the PCDD/PCDF determination is satisfactory. All the analyzed 2,3,7,8-chlorine substituted PCDD/PCDF congeners match the spiked concentrations. Here, the determination of PCDD/PCDF TEQ levels in wipe samples seems to be feasible.

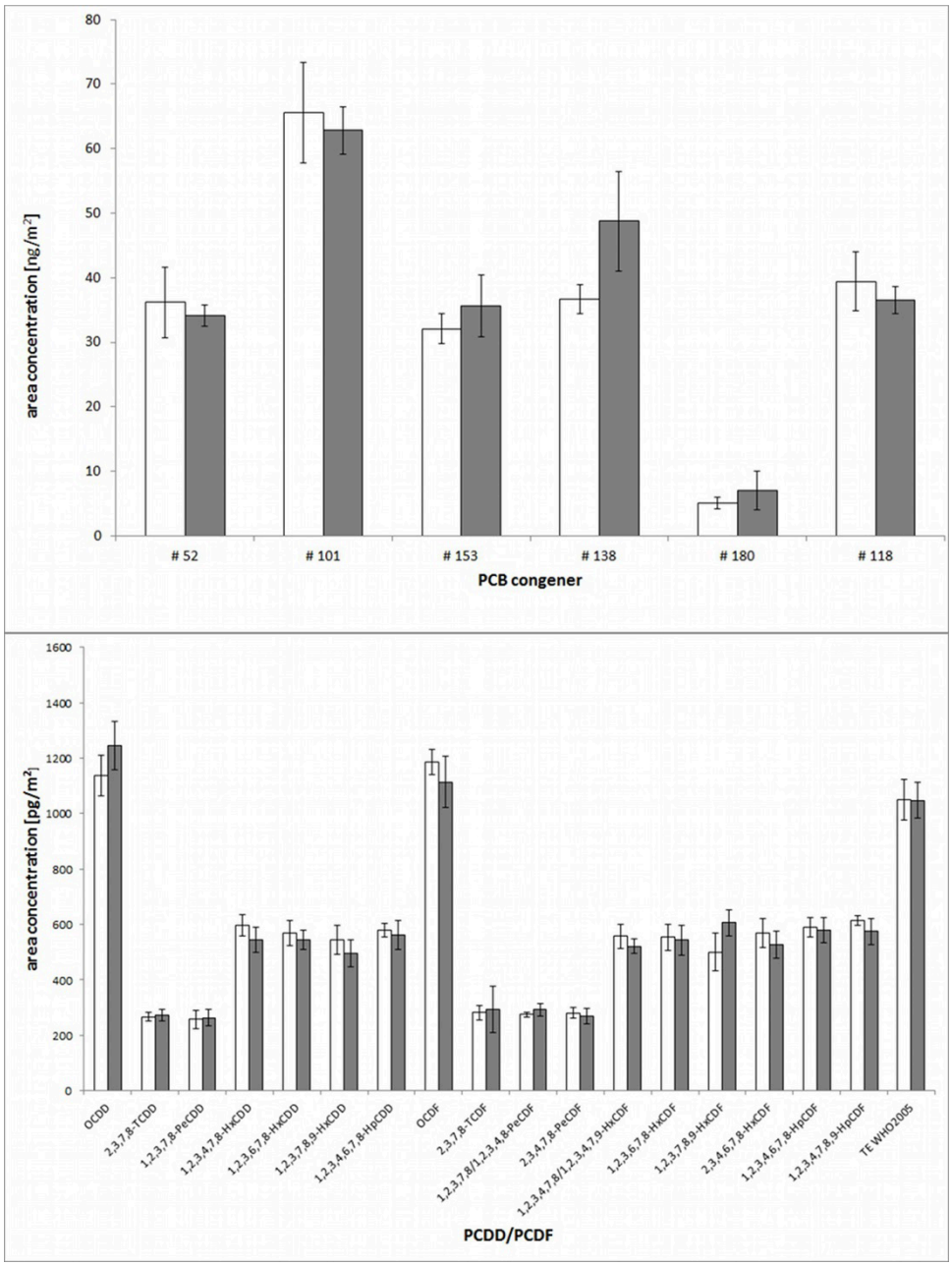


Figure 16 Upper part: Comparison of experimentally determined average area concentrations (grey bars) with the area-related certified concentrations (blank bars) using BAM CRM 5001. Lower part: Comparison of spiked PCDD/PCDF reference area concentration (blank bar) to analyzed PCDD/PCDF reference area concentrations (spotted bars). Expanded 95% confidence intervals determined in this study are additionally shown. The determination has been performed in quadruplicate.

4.3.4 Transfer efficiencies of PCBs and PCDD/PCDFs during wipe sampling

4.3.4.1 Transfer efficiencies of particulate films

As comparative value for the transfer efficiencies of PCBs and PCDD/PCDFs during wipe sampling the ratio of the analysed amount to the validated spiked amount of individual PCB or PCDD/PCDF congeners has been drawn upon. The transfer experiments had been performed in quadruplicate. For PFs all but PCB #169 could be compared. The PCB #169 concentration was below the LOD established elsewhere [Klees et al., 2015]. During this experiment 2,3,7,8-TCDD could only be determined in a single analysis, 1,2,3,7,8-PeCDD could be determined in three analyses and 1,2,3,4,7,8-HxCDD could be determined in two analyses.

A crossplot of the average analysed and average spiked reference concentrations for individual PCB and PCDD/PCDF congeners of PFs is given in **Figure 17**. Almost all PCB and PCDD/PCDF congeners were successfully removed from the testing surface and were collected via wipe sampling. Lowest transfer efficiencies were calculated for PCB #157 (89±10%) and 2,3,7,8 TCDD (50%) and highest transfer efficiencies were calculated for PCB #52 (132±28%) and 1,2,3,4,6,7,8-HpCDF (127±6%). For PCB #52, 2,3,7,8-TCDD, 1,2,3,4,6,7,8-HpCDF and OCDD deviations between analysed and average spiked reference concentrations were observed, namely. Despite the minor deviations between analysed and spiked reference concentrations, estimation of total PCB and of the toxic equivalency factor (TEQ) in wipe samples for PCDD/PCDF (101±7%) and dl-PCB (97±22%) can be performed. As the results presented in **Figure 17** reflect, sufficient transfer efficiencies for wipe sampling of PFs are already achieved with a single wiping procedure.

Altogether satisfactory transfer efficiencies of PCB and PCDD/PCDF congeners in PFs were achieved. During our experiments the limit of the uptake capacity of dust absorbed by the wipe seemed to be reached after one wiping procedure and thus further transportation to the laboratory during application to real wipe samples seemed susceptible to the loss of dust mass. However, previous investigations on PCBs in organic films on impervious urban surfaces averaged the total collected mass to 0.16 g/m^2 by weighing the wipe before and after sampling [Diamond et al., 2000]. We assume that real surface loads on impervious surfaces are in the mass range as Diamond et al. (2000) investigated. Nevertheless if sample masses appear to approximate 1g/m^2 a second wiping of the sample surface using a fresh wipe should

be considered or even better an alternative sampling technique like brushing the surface should be performed [Klees et al., 2013]. Owing to our results wiping of surfaces loaded with PFs with an organic solvent wetted cloth wipe seems to be feasible for the determination of area concentrations. It could be demonstrated, that transfer of a dust mass load of up to 1 g/m^2 from an impervious surface to an n-hexane wetted cotton cloth wipe is reproducible in one wiping procedure.

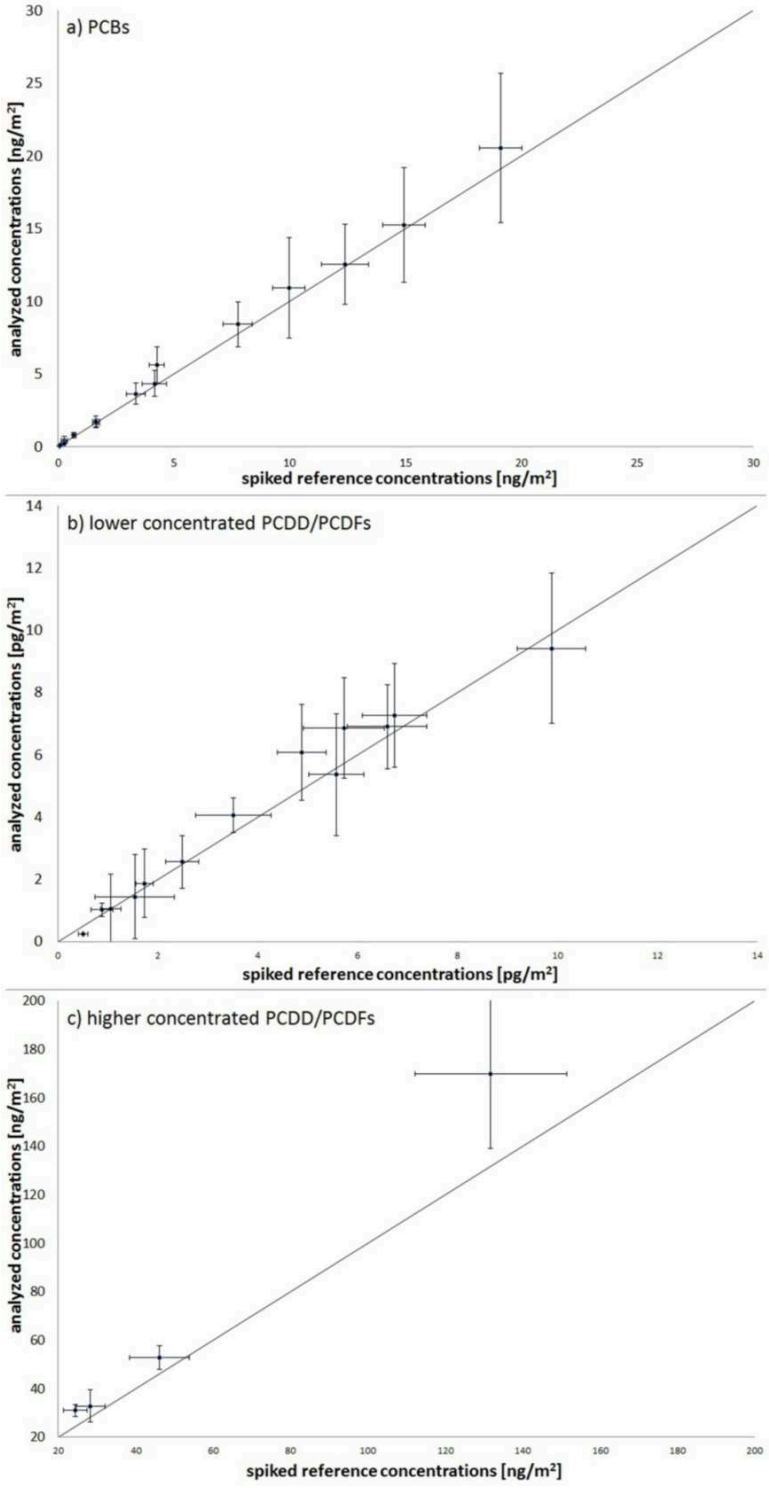


Figure 17 Comparison of spiked reference concentrations of the PCB congeners (a) and the PCDD/PCDF congeners (b) for PFs with the experimentally analyzed average. The results for higher PCDD/PCDF concentrations are enlarged in panel (c). Reference intervals (x-axis) and measured ranges (y-axis) are also shown. The diagonal 1:1 line indicates a perfect match of concentrations. Expanded 95% confidence intervals determined in this study are additionally shown. The determination was performed in quadruplicate.

4.3.4.2 Transfer efficiencies of oily liquid films

Transfer efficiencies of OFs were investigated in four individual wipes. Transfer efficiencies of PCBs and PCDD/PCDFs were calculated as the ratios of the amounts analysed on the wipe samples to the known amounts spiked onto the testing surface (n=4). For PCBs the indicator PCB #52, #101, #138, #153 and in addition the mono-ortho PCB #118 as certified in BAM CRM 5001 and for PCDD/PCDFs all 2,3,7,8 chlorine substituted congener concentrations were monitored for the calculation of transfer efficiencies. Transfer efficiencies of PCBs and PCDD/PCDFs calculated for OFs are presented in **Table 11**. Independently on the contaminant class examined in this work, transfer efficiencies were almost constant to the number of wipes as can be seen in the log-linear correlation in **Figure 18**. This observation is significant for PCDD/PCDFs and can be attributed to the noticeably lower blanks and resulting LODs for PCDD/PCDFs compared to those of PCBs. Although the results presented in **Table 11** may suggest a correlation of PCB congener specific recovery rates, one should consider that the absolute spiked amount of specific congeners certified in transformer oil BAM CRM 5001 were two times the LOD for PCB #153 and fourteen times the LOD for PCB #52. As a result of this, it cannot be ruled out that congener specific blank value effects occur during the first wipe and deviations of congener specific collection efficiencies may be ascribed to those effects. However, conclusions taken from the investigations on transfer efficiencies calculated for PCDD/PCDFs can be seen as valid. Here, spiked concentrations were up to 800 times (1,2,3,4,7,8,9-HpCDF) of the corresponding LOD.

The transfer of PCBs during the first wipe can be averaged to 73% of the total spiked area concentration (for all PCBs) using n-hexane as wetting agent to 66% of the total spiked area concentration (for all PCBs) using toluene, respectively. Average transfer efficiencies of all 17 PCDD/PCDFs congeners during the first wipe were calculated to 67% using n-heptane as wetting agent, 62% using n-hexane as wetting agent and 43% using toluene as wetting agent. This result indicated that n-heptane or n-hexane should be preferred instead of toluene as wetting agent for the collection of OFs from impervious surfaces. Furthermore, one should note that for the comparison of n-heptane to n-hexane slightly but significantly higher transfer efficiencies during the first wipe were achieved if n-heptane was used as wetting agent ($p<0.05$). For the dependency of transfer efficiency of PCDD/PCDFs in OFs using n-heptane or n-hexane as wetting agent on the number of wiping procedures a log-linear correlation was found. Indicating, that transfer efficiencies of PCDD/PCDFs in OFs for each wipe were constant independent on the number of wipes if n-heptane or n-hexane was used. The slopes

of the log-linear regression functions in **Figure 18** support our finding that transfer efficiencies of PCBs and PCDD/PCDFs in OFs are highest if n-heptane (slope: -1.02) or n-hexane (slope: -0.99) instead of toluene (slope: -0.68) is used. One should note that the steeper the negative slope of the regression function the higher the transfer efficiencies of PCBs and PCDD/PCDFs in OFs.

Nevertheless, this experiment demonstrated that the recovery rates of the spiked PCB and PCDD/PCDF concentrations were satisfactory. Furthermore, it could be demonstrated that for quantitative wipe sampling of OFs with high lipophilic content more than one wiping procedure on the sampling area is required. Depending on the collection efficiency that is regarded as sufficient for quantitative sampling, it seems not advisable to sample surface films with less than two wiping procedures.

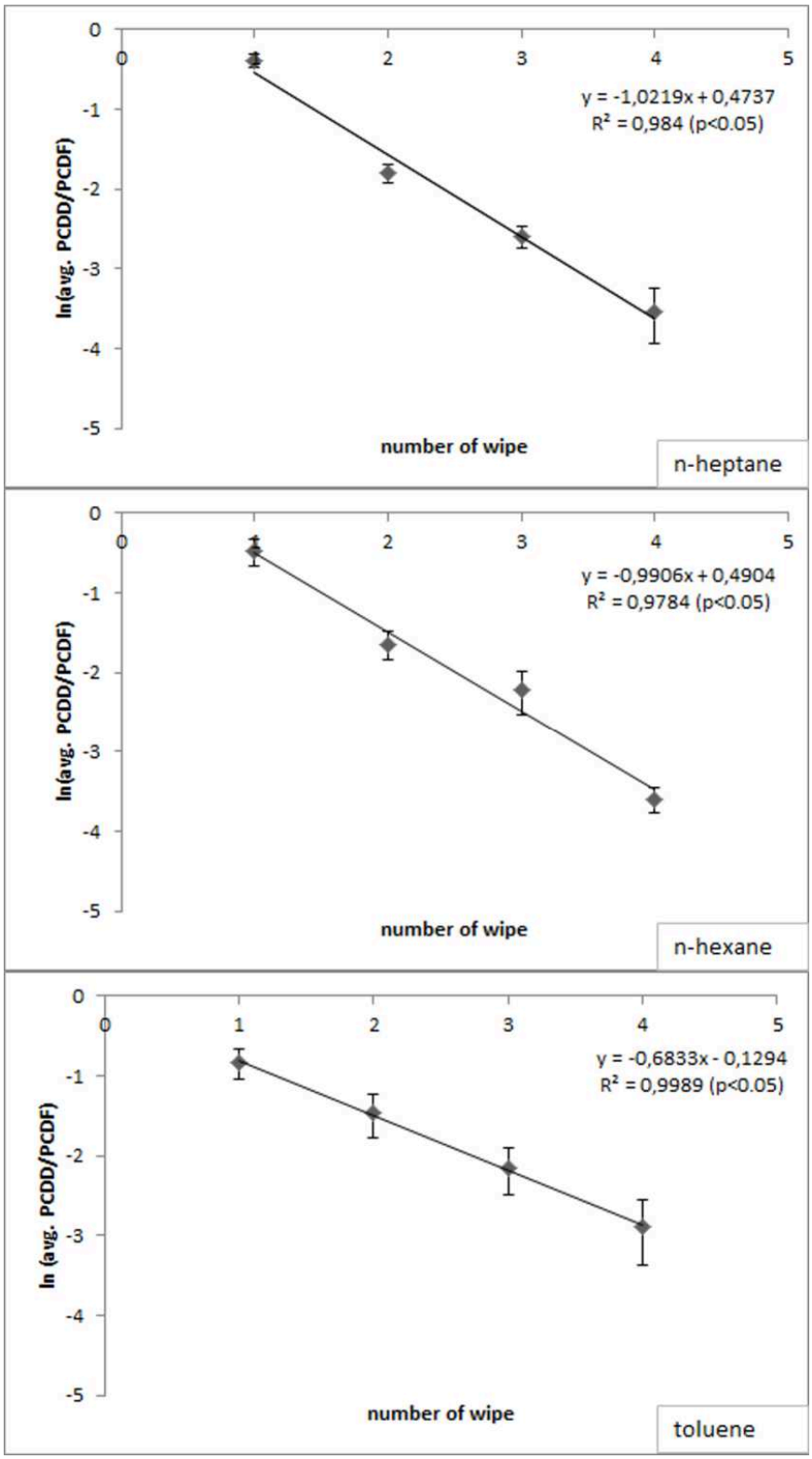


Figure 18 Dependency of concentration of all PCDD/PCDF congeners in OFs and the number of wipes using n-heptane, n-hexane and toluene as wetting agent. Standard deviations of the average transfer efficiencies calculated for all PCDD/PCDF congeners are depicted additionally. Furthermore, the linear regression model equation, the correlation coefficient and the p-value for the regression are indicated.

4.3.5 Application to real wipe samples for the determination of PCB and PCDD/PCDF area concentrations

The introduced sampling method was applied to real wipe samples collected from outdoor window surfaces (n=4), indoor environments (n=6), from surfaces of working areas and social rooms of industrial facilities sampled in cases of occupational hygiene and safety for the determination of PCBs (n=51) and in cases of environmental monitoring for the determination of PCDD/PCDF burdens after heavy accidental fires (n=13). During all of those investigations n-hexane or n-heptane were used as wetting agent for the collection of wipe samples. Based on the findings during transfer efficiency experiments at least two wiping procedures were performed during sampling. The sampling area from outdoor window surface samples can be averaged to (average ± standard error of mean) 3.54±0.42 m^2. Despite those relatively large sampling areas 92% of all PCB congener concentrations investigated were not detected. Only PCB #28 was found in all samples and PCB #77 and #126 were detected in 50% of the outdoor window surface samples analysed, respectively. During our study the total masses of organic films on window surfaces were experimentally not determined. However, as mentioned in Section **4.3.1**, if the mass loads during our study corresponded to a daily deposition load, the content of PCB in the film deposited on those window surfaces wipe sampled here were not sufficient to exceed congener specific LOQs of the present method. In contrast to the determination of PCBs, only 41% of all investigated PCDD/PCDF congeners could not be detected. Hence, application of this method for the estimation of PCDD/PCDF TEQ area concentrations on outdoor window surfaces seems to be feasible.

Furthermore, sampling areas of impervious surfaces in indoor environments of resident houses (n=6) can be averaged to 0.59±0.084 m^2. To summarize for all indoor environment wipe samples analysed 61% of all PCB congeners and 50% of all PCDD/PCDF congeners were below the sampling area dependent LOQs or LODs.

In cases of occupational hygiene and safety 0.23±0.029 m^2 were sampled in average (n=51). For those samples just 18% of all PCB congener concentrations were below the sampling area dependent LOQs. Those results confirm that the application of the introduced method in cases of occupational hygiene and safety issues as performed during the systematic survey of industrial facilities dealing in day-to-day business with PCBs is feasible. The aforementioned threshold values can be routinely monitored by using this method.

In cases of environmental monitoring for PCDD/PCDF fluxes after heavy accidental fires sampling areas (n=13) were averaged to 0.11±0.028 m^2. In addition, 57% of all PCDD/PCDF congeners were not detected. However, one should note that for 74% of all PCDD congeners and for just 45% of all PCDF congeners investigated concentrations were below the sampling area dependent LOD. LODs for individual PCDD and PCDF congeners were almost comparable. As it is known that heavy fires preferentially originate in higher PCDF contents compared to PCDD [Ruokojärvi et al., 2000], we assume that the method described here enables the evaluation of PCDD/PCDF contaminated deposition originating from heavy fires.Concentration of PCBs and PCDD/PCDFs in wipe samples

PCB in wipe samples of industrial facilities

PCB6 concentrations in wipe samples taken from surfaces of the working areas (WA) of industrial facilities (n=16) were ranging from 1.7 to 1408 µg/m^2, whereas PCB6 concentrations in the staff rooms (SR) of those industrial facilities (n=35) were ranging from 0.063 to 22 µg/m^2. A comparison of the mean PCB6 concentration in working areas and in social rooms shows that the PCB6 concentrations in the social area are significantly lower than those in the working areas (t-test $p<0.05$). Due to the lack of a toxicologically derived threshold value for PCB6 area concentrations, the guideline for the remedial action of fire damages was adopted during the systematic survey of industrial facilities. This guideline sets a threshold value for PCB6*5 of << 100 µg/m^2, corresponding to 20 µg/m^2 for PCB6 [Gesamtverband der Deutschen Versicherungswirtschaft, 2007; Schwerpunktinspektionsprogramm PCB, 2012]. The PCB6 concentration exceeds this threshold value in six of all 51 samples analysed. Five of those samples were taken from the working places, but sample TR8 was taken from a social room of a facility that is specialised on disassembling and recycling of transformers. Here a PCB6 concentration of 22 µg/m^2 was analysed that exceeds the adopted guideline value. Corresponding to the sample from the social room the wipe sample TR9 was taken from the working area of this facility and shows a PCB6 concentration of 205 µg/m^2. In addition, the information that sample TR9 was taken at ground level on the surface of a collecting drip pan located at the working area leads to the assumption that PCB can be transported e.g. from the sole of the shoes worn by the employees and consequently be carried to the social areas, where the employees recreate or even take their meals. Herein the authors see an avoidable exposure route for employees in recycling facilities that deal with toxic organic compounds. The highest value in this survey was determined in sample TR4 with a PCB6 concentration of 1407 µg/m^2. As a consequence

of detected PCB6 concentrations that were exceeding the adopted guideline value massive cleaning instructions of those subareas were initiated by the responsible. This sample was taken at a facility where the main focus is placed on the recycling of transformers.

Kuusisto et al. (2007) estimated acceptable surface concentrations for PCBs occurring in occupational scenarios on the basis of conservative assumptions of 140 µg/m^2 [Kuusisto et al., 2007]. This value was based on the determination of 15 congeners using electron capture detection or mass spectrometry. Owing to this convention for the calculation of total PCB used by Kuusisto et al. the comparison of the current data to this value is quite difficult.

Wipe samples were taken from different sectors of waste management and highest PCB6 concentrations were analysed in wipe samples with origin from the transformer recycling management. Here a mean PCB6 concentration (n=11) of 162±126 µg/m^2 (mean ± standard error of mean) was observed. As indicated in **Figure 19** the temporary deposits for hazardous waste and the metal recycling sector showed the second and third highest levels in this study. The PCB6 levels in samples from the transformer recycling sector were significantly higher compared to the other sectors analysed, whereas overlapping of PCB6 levels throughout the other datasets is noticeable (t-test $p<0.05$). Analysed PCB6 concentrations from other sectors of the waste management are summarized in **Table 12**.

Dl-PCB TEQ concentrations in surface wipe samples taken in social rooms of industrial facilities (n=34) were ranging between 0.0028 ng/m^2 and 3.2 ng/m^2. As expected, dl-PCB TEQ concentrations were elevated in wipe samples taken from the working areas (t-test $p<0.05$). Here, dl-PCB TEQ concentrations (n=16) were ranging between 0.11 ng/m^2 and 34 ng/m^2. The highest dl-PCB TEQ concentration was found for sample TR9 at the mentioned transformer recycling facility.

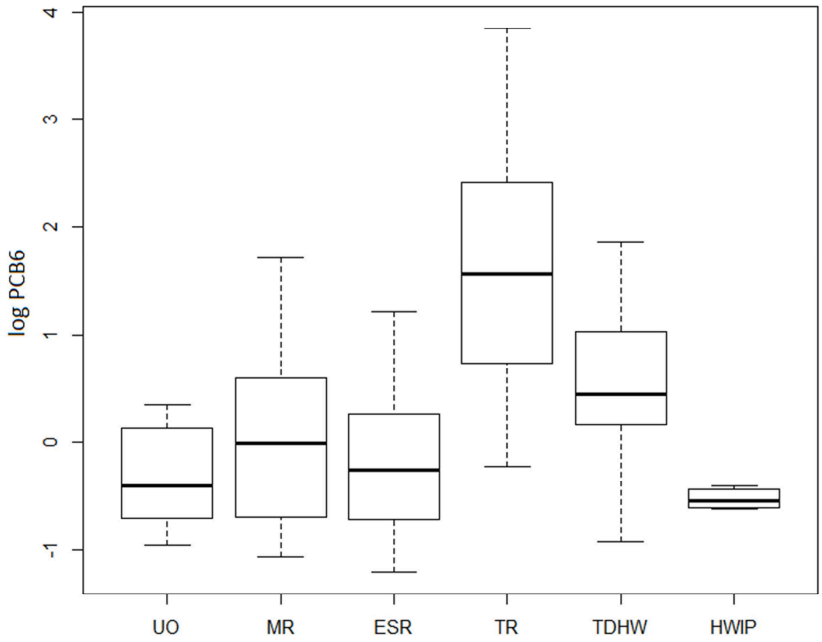


Figure 19 Boxplot of average logarithmic PCB6 concentrations in wipe samples taken from different indutrial sectors of waste mangement. UO = used oils; MR = metal recycling; ESR = electronic scrap metal; TR = transformer recycling; TDHW = temporary deposit for hazardous waste; HWIP = hazardous waste incineration plants.

PCB in wipe samples of resident houses and outdoor window surfaces

Wipe samples analysed from surfaces originating to resident houses show PCB6 levels ranging between 0.032 µg/m^2 and 0.19 µg/m^2 (n=6). All those samples exhibit PCB6 concentrations that are far from the threshold value of 20 µg/m^2 and can be classified as non-polluted. PCB6 concentrations on outdoor window surfaces were between 0.031 µg/m^2 and 0.049 µg/m^2 (n=4). Despite the fact that the sampling areas were relatively large with average sampling areas of 3.54±0.42 m^2, only PCB #28 was above the LOQ in all investigated samples. Dl-PCB TEQ concentrations were between 0.0010 ng/m^2 and 0.022 ng/m^2 in wipes from resident houses and between 0.00072 ng/m^2 and 0.00090 ng/m^2 in wipes from outdoor window surfaces.

Compared to PCB6 and dl-PCB TEQ concentrations analysed in wipes taken from surfaces of social rooms of industrial facilities, the presented concentrations in wipes from resident houses and outdoor window surfaces significantly lower and if at all equivalent.

Primarily due to the undesirable large number of congeners that were below LOQs in the current study a comparison with literature data was not performed.

PCDD/PCDF area concentrations after heavy fires

Individual concentrations of the 17 2,3,7,8-substituted PCDD/PCDF congeners and the TEQs are shown in **Table S 54** and **Table S 55**. The PCDD/PCDFs TEQ was highest with 1614 ng/m^2 for wipe sample AF10 collected from the sooty rubber profile cord ring of the face of a building downwind the fire. The PCDD/PCDF TEQ in sample AF10 indicates that during this fire a significant amount of PCDD/PCDF was emitted. For the other wipe samples analysed after heavy fires concentrations were substantially lower between 0.019 and 18 ng/m^2. In dependence on the Seveso accident from 1976, where a thermal runaway of a reactor during trichlorophenol production leaded to a massive release of PCDD/PCDFs especially 2,3,7,8-TCDD, in Germany the guidelines for restoration of fire damage sets a value of 10 ng/m^2 for permanently occupied buildings [Gesamtverband der Deutschen Versicherungswirtschaft, 2007]. This guideline value was calculated on the basis of NATO/CCMS (1988) toxicity equivalent factors (I-TEQ) [Safe, 1990]. Three of the wipe samples analysed here exceeded this guideline value. Compared to the levels Ruokojärvi et al. (2000) had analysed on impervious surfaces after the simulation of house fires that were ranging between 0.80 and 7.7 ng/m^2 similar levels of PCDD/PCDF TEQs could be analyzed on surfaces that were affected by a fire event.

PCDD/PCDF in wipe samples of resident houses and from outdoor window surfaces

PCDD/PCDF TEQs in wipe samples from surfaces of resident houses (n=6) ranged from 0.99 to 7.0 pg/m^2 and in wipe samples taken from outdoor window surfaces (n=4) from 0.45 to 1.9 pg/m^2. Those detected levels seem to represent for both indoor wipe samples from resident houses and outdoor window samples background concentrations. Despite that there is no significant difference probably due to the small amount of samples analysed, one should note that the average concentration in resident house wipe samples is higher than the average analysed on window area samples. However, the mean of the PCDD/PCDF TEQs in window

and indoor surface samples is much lower than those levels analysed after heavy fires. This observation verifies that wipe sampling is an appropriate tool for the evaluation of the input of PCDD/PCDFs to terrestrial matrices.

Table 11 PCB and PCDD/PCDF transfer efficiencies for OFs in correlation to the number of four consecutive wiping procedures (W1 to W4) using n-hexane, toluene and n-heptane as wetting agents. Experiments were performed in quadruplicate and standard deviations were given additionally.

Compounds	Transfer efficiencies in % using											
	n-hexane (n=4)				toluene (n=4)				n-heptane (n=4)			
	W1	W2	W3	W4	W1	W2	W3	W4	W1	W2	W3	W4
PCB #52	67±7	22±3	14±3	n.d.	55±10	29±6	13±1	8±1.4	n.d.	n.d.	n.d.	n.d.
PCB #101	67±7	26±2	n.d.	n.d.	57±7	32±6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB #153	75±7	n.d.	n.d.	n.d.	73±8	51±1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB #138	85±5	47±6	n.d.	n.d.	80±6	52±13	39±7	n.d.	n.d.	n.d.	n.d.	n.d.
PCB #118	71±17	22±4	n.d.	n.d.	66±23	28±5	16±1	7±1.4	n.d.	n.d.	n.d.	n.d.
2,3,7,8-TCDD	60±7	19±7	11±3	2.4±0.3	43±7	23±6	11±4	5±2	67±9	16±5	7±3	2.5±0.7
1,2,3,7,8-PeCDD	58±7	17±2	10±3	2.4±0.5	42±5	23±6	11±3	6±2	66±8	16±5	7±3	3.1±1.2
1,2,3,4,7,8-HxCDD	55±8	17±2	10±3	2.4±0.4	40±5	22±6	10±3	5±2	59±8	14±5	6±2	2.3±1.0
1,2,3,6,7,8-HxCDD	57±6	18±3	10±2	2.5±0.3	39±11	22±5	11±4	5±1.2	64±6	15±5	7±3	2.5±0.9
1,2,3,7,8,9-HxCDD	55±6	16±4	10±3	2.3±0.4	45±11	20±5	11±4	5±2	63±7	14±4	7±2	2.4±0.4
1,2,3,4,6,7,8-HpCDD	63±15	24±3	11±3	3.0±0.6	42±7	23±6	12±3	6±3	68±14	22±3	7±3	3.8±2.0
OCDD	71±35	19±3	12±3	4.1±1.2	44±7	23±7	13±2	8±5	84±32	17±7	11±2	6.5±3.9
2,3,7,8-TCDF	63±12	19±3	11±3	2.6±0.3	43±5	23±7	12±3	5±2	72±13	16±6	8±2	2.9±0.8
1,2,3,7,8-PeCDF	70±14	23±4	12±3	3.1±0.4	49±17	26±6	13±5	6±1.1	72±16	18±8	8±4	3.2±1.4
2,3,4,7,8-PeCDF	60±9	18±3	10±2	2.5±0.2	41±6	22±6	11±3	5±2	67±11	16±5	7±3	2.6±1.1
1,2,3,4,7,8-HxCDF	60±7	18±3	10±3	2.5±0.3	41±6	22±7	11±2	5±2	68±10	16±5	7±3	2.8±0.8
1,2,3,6,7,8-HxCDF	59±7	18±2	11±3	2.4±0.4	41±6	22±6	11±3	5±2	66±9	16±6	7±3	2.9±0.8
1,2,3,7,8,9-HxCDF	73±8	24±3	13±2	3.0±0.3	49±14	27±4	14±6	6±2	71±13	18±6	8±3	2.9±1.1
2,3,4,6,7,8-HxCDF	60±7	19±2	11±3	2.7±0.2	43±7	22±6	11±3	5±2	67±12	16±6	7±3	2.9±0.8
1,2,3,4,6,7,8-HpCDF	62±12	20±3	11±3	3.0±0.6	41±6	22±6	11±3	6±2	66±12	17±7	7±3	3.2±1.1
1,2,3,4,7,8,9-HpCDF	60±8	18±3	10±3	2.6±0.4	46±4	24±7	12±2	5±2	63±5	15±6	7±3	2.7±1.2
OCDF	61±11	19±4	11±3	3.1±0.4	44±7	24±6	12±3	5±2	63±10	15±6	7±3	3.2±1.6
PCDD/PCDF TEQ ½ LOD	60±7	18±2	11±3	2.4±0.3	43±7	23±6	11±3	5±2	66±9	16±5	7±3	2.7±0.9

Table 12 PCB6, dl-PCB TEQ and PCDD/PCDF TEQ levels in wipe samples investigated during the inspection of industrial facilities and after heavy fires. Ranges, means and standard errors of means and medians for all different categories are given.

	PCB6 [µg/m^2]	dl-PCB TEQ [ng/m^2]	PCDD/PCDF TEQ [ng/m^2]
Used oils (UO)			
Number of samples	5	5	-
Range	0.11-2.2	0.011-0.14	-
Mean ± standard error	0.86±0.41	0.087±0.040	-
Median	0.40	0.038	-
Metal recycling (MR)			
Number of samples	6	6	-
Range	0.055-51	0.0068-3.3	-
Mean ± standard error	9.7±8.2	0.67±0.53	-
Median	1.7	0.16	-
Electronic scrap recycling (ESR)			
Number of samples	13	13	-
Range	0.062-17	0.0086-1.3	-
Mean ± standard error	2.2±1.2	0.17±0.096	-
Median	0.56	0.069	-
Transformer recycling (TR)			
Number of samples	11	11	-
Range	0.12-1408	0.016-34	-
Mean ± standard error	162±126	8.6±4.1	-
Median	7.3	0.55	-
Temporary deposit of hazardous waste (TDHW)			
Number of samples	10	10	-
Range	0.12-73	0.0028-0.92	-
Mean ± standard error	11±7.0	0.70±0.26	-
Median	2.8	0.46	-
Hazardous waste incineration plants (HWIP)			
Number of samples	4	4	-
Range	0.24-0.40	0.021-0.049	-
Mean ± standard error	0.31±0.036	0.031±0.0063	-
Median	0.30	0.027	-
Staff room (SR)			
Number of samples	33	33	
Range	0.063-22	0.00283.2	
Mean ± standard error	1.6±0.66	0.19±0.095	
Median	0.33	0.030	

Working area (WA)			
Number of samples	16	16	
Range	1.7-1408	0.11-34	
Mean ± standard error	129±90	6.3±2.9	
Median	11	0.94	
Accidental heavy fires			
Number of samples	-	-	13
Range	-	-	0.017-1614
Mean ± standard error	-	-	127±124
Median	-	-	0.33
Resident houses (RH)			
Number of samples	4	6	6
Range	0.032-0.19	0.0010-0.022	0.00099-0.0070
Mean ± standard error	0.094±0.035	0.0071±0.0032	0.0029±0.0010
Median	0.074	0.0046	0.0020
Window surfaces (WS)			
Number of samples	4	2	4
Range	0.0062-0.0097	0.0072-0.0090	0.00045-0.0019
Mean ± standard error	0.0080±0.00089	0.00081±0.000090	0.0012±0.00030
Median	0.0081	0.00081	0.0013

4.4 Conclusion

A method for quantitative wipe sampling of surface films (PFs and OFs) for the determination of low concentrated PCBs and PCDD/PCDFs in wipe samples has been introduced. PLE has been found to be a suitable tool for the extraction of wipe tissues. Differences in transfer efficiencies with respect to the wetting solvent used for wipe sampling of OFs were observed. N-hexane and n-heptane showed highest transfer efficiencies for OFs during this study and hence are both suited to be used as wetting agents for wipe sampling. However, when authorities choose to use n-hexane as wetting solvent for sample collection, proper personal protective equipment should be worn by laboratory staff during sampling due to the possible neurotoxic character of n-hexane [Takeuchi et al., 1980; Chang, 1987].

Application to real wipe samples shows that especially wipe samples from industrial sectors analysed during the current study can exhibit PCB concentrations that may cause adverse health effects to the employees of those industrial facilities. Consequently, health effect studies of PCB area concentrations, involving hand-to-mouth, dust ingestion, inhalation and dermal ingestion are needed in order to protect employees more carefully. Furthermore, the responsible authority should pay more attention to levels of PCB on impervious surfaces and

should undertake unheralded inspections of in particular those sectors of waste management that exhibit noticeable PCB concentrations.

PCDD/PCDF area concentrations were rather low throughout this study. However, it could be demonstrated that wipe sampling is a suitable tool for the evaluation of the input of PCDD/PCDFs to terrestrial matrices originating from heavy accidental fires. This can be helpful for authorities to decide if remediation of possibly contaminated areas is needed or not.

4.5 References

BAM Polychlorierte Biphenyle in Transformatorenöl; Certificate of Analysis, 1998.

Bernard C.E., Berry M.R., Wymer L.J., Melnyk L.J. Sampling household surfaces for pesticide residues: comparison between a press sampler and solvent-moistened wipes. Sci. Total Environ. 2008, 389, 514–521.

Billets, S. A Literature Review of Wipe Sampling Methods for Chemical Warfare Agents and Toxic Industrial Chemicals. U.S. Environmental Protection Agency. EPA/600/R-07/004. 2007.

Breivik, K.; Sweetman, A.; Pacyna, J.M.; Jones, K.C. Towards a global historical emission inventory for selected PCB congeners — A mass balance approach: 1. Global production and consumption. Sci. Total Environ. 2002, 290, 181–198.

Bruckmann, P.; Hiester, E.; Klees, M.; Radermacher, L. Environmental pollution by polychlorinated biphenyls (PCB) in the harbour region of Dortmund. Gefahrst. Reinhalt. der Luft 2011, 4, 151-158.

Bruckmann, P.; Hiester, E.; Klees, M.; Zetzsch, C. Trends of PCDD/F and PCB concentrations and depositions in ambient air in Northwestern Germany. Chemosphere 2013, 93, 1471-1478.

Butt, C.M.; Diamond, M.L.; Truong, J.; Ikonomou, M.G.; Helm, P.A.; Stern, G.A. Semivolatile Organic Compounds in Window Films from Lower Manhattan after the September 11th World Trade Center Attacks. Environ. Sci. Technol. 2004, 38, 3514-3524.

Chang, Y.-C. Neurotoxic effects of n-hexane on the human central nervous system: evoked potential abnormalities in n-hexane polyneuropathy. J. Neurol. Neurosurg. Psychiatry 1987, 50, 269-274.

Deziel, N.C.; Viet, S.M.; Rogers, J.W.; Camann, D.E; Marker, D.A.; Heikkinen, M.S.A.; Yau, A.Y.; Stout II, D.M.; Dellarco, M. Comparison of wipe materials and wetting agents for pesticide residue collection from hard surfaces. Sci. Total Environ. 2011, 409, 4442-4448.

Diamond, M.L.; Gingrich S.E.; Fertuck, K.; McCarry, B.E.; Stern, G.A.; Billeck, B.; Grift, B.; Brooker, D.; Yager, T.D. Evidence for Organic Film on an Impervious Urban Surface: Characterization and Potential Teratogenic Effects. Environ. Sci. Technol. 2000 34, 2900-2908.

Eitzer, B.D; Hites, R.A. Atmospheric Transport and Deposition of Polychlorinated Dibenzo-p-dioxins and –benzofurans. Environ. Sci. Technol. 1989, 23, 1396-1401.

Frame, G. M. A collaborative study of 209 PCB congeners and 6 Aroclors on 20 different HRGC columns: 1. Retention and coelution database. Fresenius J. Anal. Chem. 1997, 357, : 701–713.

Gesamtverband der Deutschen Versicherungswirtschaft (Hrsg.): Richtlinien zur Brandschadensanierung, VDS 2357, VDS Schadenverhütung GmbH, Köln, 2007.

Gingrich S.E., Diamond, M.L., Stern, G.A., McCarry, B.E. Atmospherically Derived Organic Surface Films along an Urban-Rural Gradient. Environ. Sci. Technol. 2001, 35, 4031-4037.

Klees, M.; Hiester, E.; Bruckmann, P.; Schmidt, T.C. Determination of polychlorinated biphenyls and polychlorinated dibenzo-p-dioxins and dibenzofurans by pressurized liquid extraction and gas chromatography coupled to mass spectrometry in street dust samples. J. Chromatogr. A 2013, 1300, 17-23.

Klees, M.; Hiester, E.; Bruckmann, P.; Molt, K.; Schmidt, T.C. Polychlorinated biphenyls and polychlorinated dibenzo-p-dioxins and dibenzofurans in street dust of North-Rhine Westphalia, Germany. Sci. Total Environ. 2015, 511, 72-81.

Kuusisto, S., Lindroos, O., Rantio, T., Priha, E., Tuhkanen, T. PCB contaminated dust on indoor surfaces – Health risks and acceptable surface concentrations in residential and occupational settings. Chemosphere 2007, 67, 1194-1201.

LANUV. http://www.lanuv.nrw.de/luft/immissionen/staub/messergeb.htm; 19.12.2014.

Law, N.L; Diamond, M.L. The role of organic films and the effect of hydrophobic organic compounds in urban areas: An hypothesis. Chemosphere 1998, 36, 2607-2620.

Lioy, P.J., Freeman, N.C.G., Millette, J.R. Dust: A Metric for Use in Residential and Building Exposure Assessment and Source Characterization. Environ. Health Perspect. 2002, 110, 969–983.

Loos, R.; Vollmuth, S.; Niessner, R. Group separation of ortho-PCBs, coplanar non-ortho–PCBs and PCDDs/PCDFs using an alumina column as an one-step clean-up procedure. Fresenius J. Anal. Chem., 1997, 357, 1081-1087.

Petroleum products and used oils. Determination of PCBs and related products.Part 2: Calculation of polychlorinated biphenyl (PCB) content; German version EN 12766-2:2001.

R., 2013. A Language and Environment for Statistical Computing, R Foundation for Statistical Computing, Vienna 2013. (www.r-project.org).

Ruokojärvi, P.; Aatamila, M.; Ruuskanen, J. Toxic chlorinated and polyaromatic hydrocarbons in simulated house fires. Chemosphere 2000, 41, 825-828.

Safe, S. Polychlorinated Biphenyls (PCBs), Dibenzo-p-Dioxins (PCDDs), Dibenzofurans (PCDFs), and Related Compounds: Environmental and Mechanistic Considerations Which Support the Development of Toxic Equivalency Factors (TEFs). Crit. Rev. Toxicol., 1990, 20, 51-88.

Schwerpunktinspektionsprogramm PCB. Inspektion von Anlagen, in denen PCB-haltiger-Abfall anfällt oder entsorgt wird. LANUV-Fachbericht 39. ISSN 1864-3930 LANUV-Fachberichte. 2012.

Stapleton, H.M.; Kelly, S.M.; Allen, J.G.; McClean, M.D.; Webster, T.F. Measurement of Polybrominated Diphenyl Ethers on Hand Wipes: Estimating Exposure from Hand-to-Mouth Contact. Environ. Sci. Technol. 2008, 42, 3329–3334.

Stout II, D.M.; Bradham, K.D.; Egeghy, P.P.; Croghan, C.W.; Ashley, P.A.; Pinzer, E.; Friedman, W.; Brinkman, M.C.; Nishioka, M.G. Cox, D.C. American Healthy Homes Survey: A National Study of Residential Pesticides Measured from Floor Wipes. Environ. Sci. Technol. 2009, 43, 4294–4300.

Takeuchi, Y., Ono, Y., Hisanaga, N., Kitoh, J., Sugiura, Y. A comparative study on the neurotoxicity of n-pentane, n-hexane, and n-heptane in the rat. Br. J. Ind. Med. 1980, 37, 241-247.

Testing and Quality Assurance Plan for the Evaluation of Wipe Sampling Methods for Collecting Chemical Warfare Agents (CWAs), CWA Degradation Products, and Toxic Industrial Chemicals from Various Surfaces. United States Environmental Protection Agency. EPA/600/R-08/079 February 2008.

Toms, L.-M.L.; Bartkow, M.E.; Symons, R.; Paepke, O.; Mueller, J.F. Assessment of polybrominated diphenyl ethers (PBDEs) in samples collected from indoor environments in South East Queensland, Australia. Chemosphere 2009, 76, 173–178.

UNEP, 2007. Guidance on the Global Monitoring Plan for Persistent Organic Pollutants. UNEP/CHEMICALS/2007/2.

Wobst, M., Wichmann, H., Bahadir, M. Surface contamination with PASH, PAH and PCDD/F after fire accidents in private residences. Chemosphere 1999, 38, 1685-1691.

Wu, R.W., Harner, T., Diamond, M.L. Evolution rates and PCB content of surface films that develop on impervious urban surfaces. Atmos. Environ. 2008, 42, 6131–6143.

4.6 Supporting Information

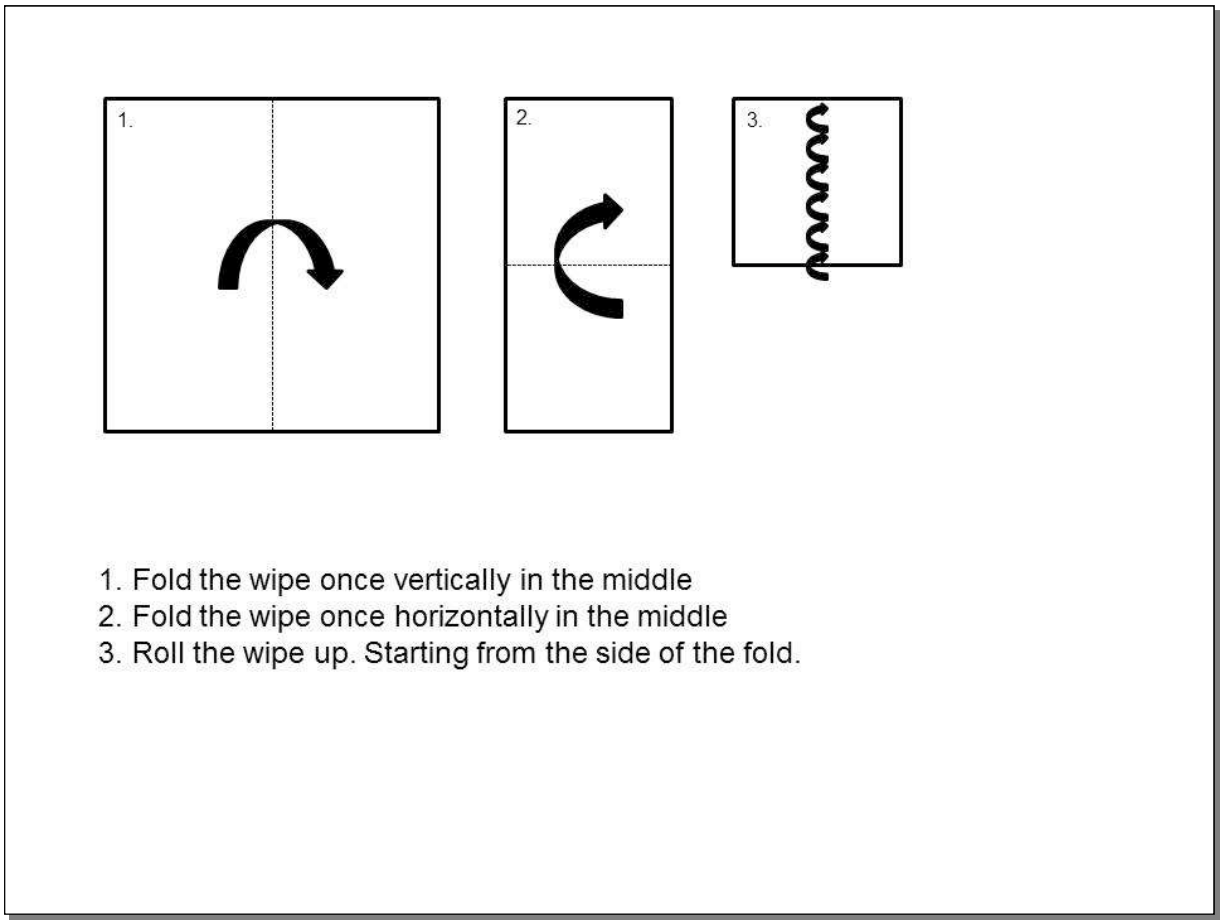
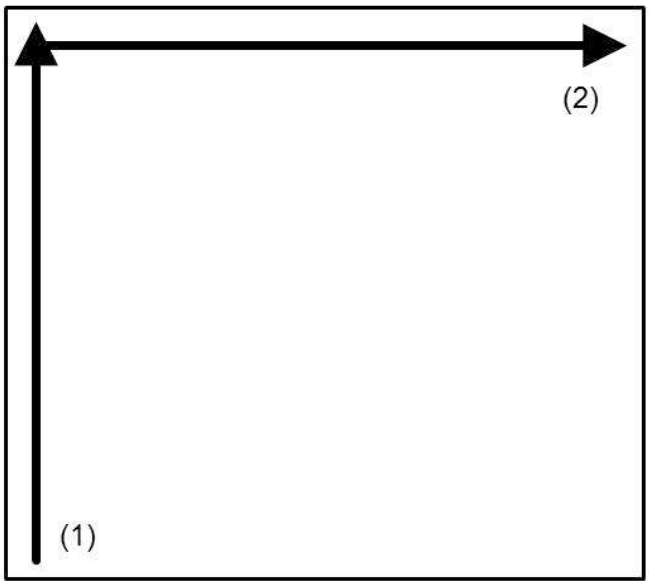


Figure S 30 Folding scheme for the PLE of wipe samples



1. The model surface has to wiped completely in vertical (1) direction
2. The model surface has to wiped completely in horizontal (2) direction

Figure S 31 Wiping scheme during wipe sample collection

Table S 31 m/z ratios for the determination of HpCDD/CDF and OCDD/CDF congeners and homologues. D/F6=HxCDD/HxCDF; D/F7=HpCDD/HpCDF; D/F8=OCDD/OCDF; n= native congener

lock mass	cali mass	Comp.	target mass	ratio mass	cycle time sec
366.9787	404.9755	F6 n	373.8202	375.8172	**0.6**
		F6 ^{13}C	385.8604	387.8575	
		D6 n	389.8151	391.8122	
		D6 ^{13}C	401.8555	403.8524	
404.9755	455.9757	F7 n	407.7812	409.7783	**0.6**
		F7 ^{13}C	419.8215	421.8185	
		D7 n	423.7761	425.7732	
		D7 ^{13}C	435.8164	437.8134	
455.9757	492.9691	F8 n	441.7422	443.7393	**0.6**
		F8 ^{13}C	453.7825	455.7796	
		D8 n	457.7372	459.7342	
		D8 ^{13}C	469.7774	471.7745	

Table S 32 m/z ratios for the determination of non-ortho PCBs. P4=TetrachloroBP; P5=PentachloroBP; P6=HexachloroBP; n= native congener

lock mass	cali mass	Comp.	target mass	ratio mass	cycle time sec
292.9818	316.9819	P4 n	289.9218	291.9189	**0.7**
		P4 ^{13}C	301.9621	303.9591	
316.9819	366.9787	P5 n	325.8799	327.8769	**0.6**
		P5 ^{13}C	337.9202	339.9172	
366.9787	404.9755	P6 n	359.8409	361.8380	**0.5**
		P6 ^{13}C	371.8812	373.8782	

Table S 33 m/z ratios for the determination of indicator and mono-ortho PCBs. P4=TetrachloroBP; P5=PentachloroBP; P6=HexachloroBP; P7=HeptachloroBP; P8=OctachloroBP; P9=NonachloroBP; P10=DecachloroBP; n= native congener

lock mass	cali mass	Comp.	target mass	ratio mass	cycle time sec
242.9851	316.9819	P3 n	255.9608	257.9578	**0.6**
		P3^{13}C	268.0010	269.9981	
		P4 n	289.9218	291.9189	
		P4 ^{13}C	301.9621	303.9591	
		P5 n	325.8799	327.8769	
		P5 ^{13}C	337.9202	339.9172	
292.9819	366.9787	P4 n	289.9218	291.9189	**0.7**
		P4 ^{13}C	301.9621	303.9591	
		P5 n	325.8799	327.8769	
		P5 ^{13}C	337.9202	339.9172	
		P6 n	359.8409	361.8380	
		P6 ^{13}C	371.8812	373.8782	
316.9819	404.9755	P5 n	325.8799	327.8769	**0.8**
		P5 ^{13}C	337.9202	339.9172	
		P6 n	359.8409	361.8380	
		P6 ^{13}C	371.8812	373.8782	
		P7 n	393.8019	395.7990	
		P7 ^{13}C	405.8422	407.8392	
366.9787	454.9723	P6 n	359.8409	361.8380	**0.9**
		P6 ^{13}C	371.8812	373.8782	
		P7 n	393.8019	395.7990	
		P7 ^{13}C	405.8422	407.8392	
		P8 n	427.7630	429.7600	
		P8 ^{13}C	439.8032	441.8003	
404.9755	454.9723	P7 n	393.8019	395.7990	**0,9**
		P7 ^{13}C	405.8422	407.8392	
		P8 n	427.7630	429.7600	
		P8 ^{13}C	439.8032	441.8003	
		P9 n	461.7240	463.7210	
		P9 ^{13}C	473.7643	475.7613	
454.9723	504.9691	P10 n	497.6821	499.6791	**1.1**
		P10 ^{13}C	509.7223	511.7194	

Table S 34 Concentrations and confidence intervals for PCB and PCDD/PCDF homologues and congeners in the spiking surrogate for PFs

	concentration	95% confidence interval
PCB homologues	**(µg/kg)**	**(µg/kg)**
TriPCBs	12	1.4
TetraPCBs	69	8.6
PentaPCBs	65	4.1
HexaPCBs	72	4.0
HeptaPCBs	38	5.3
OctaPCBs	8.7	1.0
NonaPCBs	0.44	0.18
DecaPCB	0.15	0.029
PCB congeners	**(µg/kg)**	**(µg/kg)**
PCB #28	3.3	0.41
PCB #52	4.3	0.33
PCB #101	10	0.69
PCB #153	15	0.91
PCB #138	19	0.92
PCB #180	12	1.0
PCB #81	0.073	0.0075
PCB #77	1.6	0.15
PCB #126	0.11	0.012
PCB #169	0.013	0.0024
PCB #123	0.26	0.13
PCB #118	7.8	0.63
PCB #114	0.25	0.059
PCB #105	4.2	0.53
PCB #167	0.68	0.096
PCB #156	1.6	0.16
PCB #157	0.25	0.036
PCB #189	0.26	0.036
TEQ excl. LOD	0.012	0.0013
TEQ ½ LOD	0.012	0.0013
TEQ incl. LOD	0.012	0.0013
PCDD/PCDF homologues	**(ng/kg)**	**(ng/kg)**
TCDD	12	3.2
PCDD	25	8.1
HxCDD	41	8.8
HpCDD	56	9.8
OCDD	132	25
TCDF	91	13
PCDF	77	11
HxCDF	68	13
HpCDF	41	7.1
OCDF	46	9.7
PCDD/PCDF congeners	**(ng/kg)**	**(ng/kg)**
2,3,7,8-TCDD	0.46	0.17
1,2,3,7,8-PeCDD	0.88	0.27
1,2,3,4,7,8-HxCDD	1.0	0.26
1,2,3,6,7,8-HxCDD	2.5	0.41
1,2,3,7,8,9-HxCDD	1.7	0.22
1,2,3,4,6,7,8-HpCDD	28	4.7
2,3,7,8-TCDF	4.9	0.61
1,2,3,7,8-PeCDF	5.7	1.0
2,3,4,7,8-PeCDF	5.6	0.69
1,2,3,4,7,8-HxCDF	6.7	0.81
1,2,3,6,7,8-HxCDF	6.6	0.99
1,2,3,7,8,9-HxCDF	1.5	1.00
2,3,4,6,7,8-HxCDF	9.9	0.87
1,2,3,4,6,7,8-HpCDF	24	3.8
1,2,3,4,7,8,9-HpCDF	3.5	0.95
TEQ excl. LOD	7.3	0.98
TEQ ½ LOD	7.3	0.96
TEQ incl. LOD	7.3	0.96

Table S 35 Analysed concentrations for individual PCB and PCDD/PCDF congeners during the spiking experiment for PFs

	PF1	PF2	PF3	PF4
PCB congeners	**(µg/kg)**	**(µg/kg)**	**(µg/kg)**	**(µg/kg)**
PCB #28	3.7	4.0	3.5	3.4
PCB #52	5.2	6.6	5.6	5.0
PCB #101	12	13	10.0	9.0
PCB #153	17	16	14	13
PCB #138	22	21	20	18
PCB #180	13	13	12	11
PCB #81	0.061	0.072	0.064	0.065
PCB #77	1.5	1.8	1.5	1.64
PCB #126	0.10	0.12	0.093	0.10
PCB #169	0.010	0.012	0.0096	0.011
PCB #123	0.50	0.57	0.55	0.25
PCB #118	8.5	9.1	8.0	8.0
PCB #114	0.27	0.30	0.252	0.24
PCB #105	4.3	4.9	4.1	4.0
PCB #167	0.83	0.91	0.76	0.73
PCB #156	1.8	1.8	1.7	1.5
PCB #157	0.25	0.28	0.25	0.22
PCB #189	0.26	0.28	0.23	0.23
	PF1	PF2	PF3	PF4
PCDD/PCDF congeners	**(ng/kg)**	**(ng/kg)**		
2,3,7,8-TCDD	-	-	-	0.26
1,2,3,7,8-PeCDD	0.79	-	1.2	0.26
1,2,3,4,7,8-HxCDD	1.4	-	0.60	
1,2,3,6,7,8-HxCDD	2.9	2.8	2.6	1.9
1,2,3,7,8,9-HxCDD	1.7	2.6	2.2	0.9
1,2,3,4,6,7,8-HpCDD	31	37	30	34
OCDD	159	192	177	174
1,2,3,7,8-PeCDF	6.2	5.7	5.3	6.9
2,3,4,7,8-PeCDF	6.3	6.2	9.0	7.9
1,2,3,4,7,8-HxCDF	6.0	6.1	5.1	4.0
1,2,3,6,7,8-HxCDF	7.1	8.0	6.3	7.3
1,2,3,7,8,9-HxCDF	6.6	7.2	6.1	7.6
2,3,4,6,7,8-HxCDF	2.1	1.7	1.6	0.3
1,2,3,4,6,7,8-HpCDF	9.0	11	8.6	8.5
1,2,3,4,7,8,9-HpCDF	29	32	32	30
2,3,7,8-TCDD	4.0	3.8	4.7	4.3
OCDF	47	54	61	48

Table S 36 Concentrations and confidence intervals for PCB and PCDD/PCDF homologues and congeners in the spiking surrogate for OFs

	concentration	95% confidence interval
PCB congeners	**(µg/kg)**	**(µg/kg)**
PCB #52	0.79*	0.12*
PCB #101	1.4*	0.17*
PCB #153	0.70*	0.10*
PCB #138	0.80*	0.050*
PCB #180	0.11*	0.020*
PCB #118	0.86*	0.10*
PCB #28	0.0083	0.0035
PCB #81	0.00013	0.000044
PCB #77	0.0033	0.000076
PCB #126	0.00083	0.000091
PCB #169	0.000034	0.0000078
PCB #123	0.030	0.0063
PCB #114	0.016	0.0041
PCB #105	0.24	0.014
PCB #167	0.036	0.0024
PCB #156	0.081	0.0062
PCB #157	0.015	0.00092
PCB #189	0.0028	0.00033
PCDD/PCDF homologues	**(pg/µl)**	**(pg/µl)**
TCDD	-	-
PCDD	-	-
HxCDD	-	-
HpCDD	-	-
OCDD	23	1.5
TCDF	-	-
PCDF	-	-
HxCDF	-	--
HpCDF	-	-
PCDD/PCDF congeners	**(pg/µl)**	**(pg/µl)**
2.3.7.8-TCDD	5.3	0.31
1.2.3.7.8-PeCDD	5.1	0.66
1.2.3.4.7.8-HxCDD	12	0.76
1.2.3.6.7.8-HxCDD	11	0.92
1.2.3.7.8.9-HxCDD	11	1.1
2.3.7.8-TCDF	5.6	0.52
1.2.3.7.8-PeCDF	5.5	0.19
2.3.4.7.8-PeCDF	5.6	0.40
1.2.3.4.7.8-HxCDF	11	0.86
1.2.3.6.7.8-HxCDF	11	0.94
1.2.3.7.8.9-HxCDF	10	1.4
2.3.4.6.7.8-HxCDF	11	1.1
1.2.3.4.6.7.8-HpCDF	12	0.71
TEQ excl. LOD	21	1.5
TEQ ½ LOD	21	1.5
TEQ incl. LOD	21	1.5

*= taken from BAM CRM 5001 Certificate of Analysis

Table S 37 Determination of the density of BAM CRM 5001. Individual mass determination (n=10) are depicted. Furthermore the calculated density plus standard deviation is shown.

No.	Mass [g]	Density [g/µL]
1	0.04568	
2	0.04544	
3	0.04646	
4	0.04579	
5	0.04576	
6	0.0462	
7	0.04501	
8	0.0464	
9	0.04616	
10	0.04521	
Average		0.000916±0.000494

Table S 38 Recovery rates of individual $^{13}C_{12}$ quantification standards after Soxhlet

	SOX1	SOX2	SOX3	SOX4	SOX5	SOX6	SOX7	SOX8	SOX9	SOX10	SOX11	SOX12	SOX13	SOX14	SOX15	SOX16	SOX17	SOX18	SOX19
PCB #28	70	61	87	70	63	84	96	89	83	81	87	31	44	102	47	34	22	79	85
PCB #52	64	65	86	75	72	80	90	86	76	80	78	25	36	89	60	47	19	75	83
PCB #101	60	64	79	77	84	69	77	91	76	74	69	26	31	80	79	62	15	77	77
PCB #123	62	76	90	100	113	80	91	92	76	92	86	30	38	94	91	77	14	63	55
PCB #118	62	75	90	91	85	73	81	92	76	82	84	26	34	84	83	73	14	61	56
PCB #114	66	79	91	95	98	75	87	96	78	86	86	28	36	86	137	77	14	81	73
PCB #105	63	78	89	92	94	76	86	93	79	86	86	29	37	88	79	77	16	81	73
PCB #153	56	73	87	88	96	66	78	92	73	83	82	25	32	87	83	76	13	81	72
PCB #138	61	78	90	93	96	63	81	92	72	77	85	24	30	84	78	80	13	78	72
PCB #167	51	72	82	88	95	62	73	84	69	77	80	23	29	82	69	70	10	77	72
PCB #156	50	73	82	82	105	63	73	89	71	79	83	24	30	78	74	75	12	70	64
PCB #157	50	72	81	79	108	63	72	89	70	79	81	25	33	80	77	75	11	70	65
PCB #180	39	61	67	71	75	50	61	82	64	70	67	20	25	74	65	65	8	71	67
PCB #189	37	64	65	71	76	50	58	74	57	69	70	25	28	73	68	66	8	57	54
PCB #194	25	61	62	63	65	43	51	67	52	60	65	22	27	73	71	66	8	74	66
PCB #208	33	60	66	66	70	44	54	71	53	65	66	21	16	72	75	65	8	65	59
PCB #209	25	52	49	48	51	32	37	56	43	51	54	20	9	64	69	57	5	49	48

Table S 39 Recovery rates of individual $^{13}C_{12}$ quantification standards after Soxhlet

	SOX20	SOX21	SOX22	SOX23	SOX24	SOX25	SOX26	SOX27	SOX28	SOX29	SOX30	SOX31	SOX32	SOX33	SOX34	SOX35	SOX36
PCB #28	79	75	67	70	63	88	74	73	91	56	30	101	98	91	68	31	10
PCB #52	75	62	70	74	63	62	70	83	88	63	26	93	88	91	60	29	10
PCB #101	72	63	69	74	63	74	69	79	83	74	20	93	78	83	54	26	10
PCB #123	59	52	78	84	73	85	78	94	93	83	19	90	83	94	59	27	13
PCB #118	54	50	75	82	70	82	77	88	94	77	21	88	84	90	56	27	11
PCB #114	71	71	76	82	70	88	79	92	96	84	20	93	86	92	57	28	12
PCB #105	74	77	76	83	73	90	78	87	88	82	22	88	83	92	59	27	12
PCB #153	70	67	72	80	70	87	79	90	95	77	17	85	79	88	53	26	11
PCB #138	73	66	74	82	69	95	86	83	99	70	18	80	87	91	55	24	10
PCB #167	70	63	62	70	68	80	77	79	82	73	17	78	68	74	45	21	9
PCB #156	66	72	66	72	69	92	81	80	84	73	15	76	71	77	46	21	9
PCB #157	65	68	65	72	69	86	79	81	84	72	15	75	71	78	48	22	9
PCB #180	66	65	52	57	61	75	70	73	75	66	11	71	57	63	37	17	8
PCB #189	77	59	50	52	67	80	75	73	77	64	11	60	53	56	32	16	10
PCB #194	69	66	44	47	66	60	54	84	57	68	10	53	37	51	28	14	9
PCB #208	44	42	47	51	71	77	68	85	73	60	10	56	48	49	33	17	8
PCB #209	20	22	33	35	53	67	48	71	44	39	9	43	35	20	22	11	6

Table S 40 Recovery rates of individual $^{13}C_{12}$ quantification standards after Soxhlet

	SOX37	SOX38	SOX39	SOX40	SOX41	SOX42	SOX43	SOX44	SOX45	SOX46	SOX47	SOX48	SOX49	SOX50	SOX51
PCB #28	25	87	64	32	120	74	49	55	108	47	82	69	97	-	
PCB #52	30	87	60	33	114	77	58	60	101	45	90	72	81	113	75
PCB #101	25	91	52	27	104	72	60	64	91	44	88	77	85	122	57
PCB #123	33	92	59	35	102	89	75	75	100	47	79	79	88	-	55
PCB #118	29	90	57	31	99	77	70	75	95	45	79	76	79	-	95
PCB #114	29	93	61	35	99	87	74	75	99	45	83	77	87	-	83
PCB #105	30	90	61	33	98	86	79	81	97	46	88	81	89	-	114
PCB #153	27	87	53	29	100	82	75	76	91	42	77	79	86	124	57
PCB #138	26	87	53	28	99	88	77	78	95	42	74	78	85	129	58
PCB #167	24	80	51	28	90	83	73	72	74	41	68	71	84	107	55
PCB #156	21	83	53	29	89	84	77	79	78	41	78	80	91	125	77
PCB #157	23	83	53	28	80	83	79	77	78	42	71	78	89	97	43
PCB #180	19	72	42	23	74	74	68	68	63	36	54	78	83	84	39
PCB #189	23	64	43	23	74	85	79	70	54	35	47	67	74	72	29
PCB #194	24	53	38	20	86	83	78	71	50	29	40	68	70	57	32
PCB #208	22	61	37	22	63	82	82	70	54	30	47	60	62	76	34
PCB #209	15	43	29	16	31	73	70	58	34	25	30	52	34	50	18

Table S 41 Recovery rates of individual $^{13}C_{12}$ quantification standards after PLE

	PLE1	PLE2	PLE3	PLE4	PLE5	PLE6	PLE7	PLE8	PLE9	PLE10	PLE11	PLE12	PLE13	PLE14	PLE15	PLE16	PLE17	PLE18	PLE19	PLE20
PCB #28	39	42	54	54	58	60	58	59	51	54	56	62	59	72	45	54	92	84	78	54
PCB #52	46	42	50	49	55	60	55	57	48	53	54	62	59	69	50	57	85	79	72	54
PCB #101	53	56	59	56	59	64	61	63	54	59	57	65	61	75	63	72	95	89	82	60
PCB #123	60	58	66	65	61	65	64	65	58	64	60	70	61	77	70	80	93	90	83	62
PCB #118	57	56	64	60	60	65	63	63	57	63	60	68	58	73	68	78	92	86	80	60
PCB #114	65	63	70	68	65	68	66	67	67	70	64	71	63	78	71	81	96	93	87	65
PCB #105	59	59	64	63	61	62	63	64	64	67	60	68	62	76	67	76	92	88	81	59
PCB #153	60	57	62	59	59	62	61	63	60	63	58	66	57	71	68	78	87	83	78	58
PCB #138	61	60	65	62	60	64	64	65	63	66	59	67	59	73	69	81	90	86	81	62
PCB #167	60	58	64	58	56	61	61	61	62	63	56	64	61	78	67	75	82	79	75	57
PCB #156	76	72	77	71	68	67	68	67	68	70	62	71	65	79	74	85	92	89	83	62
PCB #157	77	75	79	73	69	68	69	69	71	70	64	72	65	81	73	85	92	91	85	64
PCB #180	61	57	62	56	57	61	61	61	60	60	55	62	57	71	66	77	77	75	72	55
PCB #189	79	74	80	72	69	68	69	67	70	69	64	71	68	83	74	85	84	84	78	59
PCB #194	66	69	70	64	55	60	63	59	60	60	59	62	55	70	62	74	69	68	63	54
PCB #208	62	61	65	57	57	54	53	61	59	58	53	60	55	64	66	76	73	69	64	54
PCB #209	55	55	56	54	40	32	28	58	55	56	56	58	46	40	52	68	58	59	57	50

Table S 42 Recovery rates of individual $^{13}C_{12}$ quantification standards after PLE

	PLE21	PLE22	PLE23	PLE24	PLE25	PLE26	PLE27	PLE28	PLE29	PLE30	PLE31	PLE32	PLE33	PLE34	PLE35	PLE36
PCB #28	146	100	126	136	47	64	70	66	52	68	72	78	67	73	73	62
PCB #52	117	79	99	115	46	64	69	63	47	63	69	77	62	66	69	60
PCB #101	97	69	91	101	48	71	74	65	57	73	73	80	70	74	76	67
PCB #123	92	64	80	93	54	75	77	68	39	77	74	80	46	80	81	70
PCB #118	90	65	79	88	52	72	75	66	78	76	75	80	42	102	78	68
PCB #114	84	66	80	86	54	76	78	68	67	80	77	82	74	82	84	72
PCB #105	81	62	76	82	49	68	70	61	64	75	71	77	73	79	79	71
PCB #153	82	60	73	85	53	73	76	66	63	75	72	77	67	72	75	66
PCB #138	81	56	73	81	53	74	76	66	65	80	72	79	70	75	79	71
PCB #167	69	55	66	67	45	63	64	54	60	72	68	71	63	66	33	63
PCB #156	74	56	74	71	54	80	78	64	71	82	73	77	73	78	80	70
PCB #157	80	65	93	72	53	83	74	63	70	81	73	76	77	83	82	72
PCB #180	71	57	71	69	49	72	68	57	58	68	63	66	64	68	70	63
PCB #189	69	53	72	66	53	80	74	61	66	77	68	70	71	83	78	67
PCB #194	58	53	68	65	47	73	68	56	64	67	64	64	64	73	68	63
PCB #208	62	53	72	63	48	72	69	57	62	69	64	66	61	71	68	60
PCB #209	46	38	59	56	45	61	65	53	61	61	61	63	64	69	62	55

Table S 43 Recovery rates of individual $^{13}C_{12}$ quantification standards after PLE

	PLE37	PLE38	PLE39	PLE40	PLE41	PLE42	PLE43	PLE44	PLE45	PLE46
PCB #28	52	57	53	53	38	82	21	68	69	80
PCB #52	53	59	55	54	45	108	39	83	86	108
PCB #101	56	63	55	56	21	57	37	42	43	58
PCB #123	62	69	60	60	18	47	36	35	33	48
PCB #118	60	68	58	59	17	44	36	33	31	45
PCB #114	62	71	60	61	18	47	38	36	35	51
PCB #105	61	69	59	61	20	52	41	40	38	52
PCB #153	60	67	56	58	27	77	60	54	50	78
PCB #138	61	69	58	60	27	78	62	56	51	79
PCB #167	57	66	55	55	29	83	68	60	53	82
PCB #156	63	71	62	59	19	59	49	41	39	58
PCB #157	71	74	67	62	18	58	47	41	38	58
PCB #180	63	72	61	61	25	85	70	59	49	81
PCB #189	69	75	63	61	17	60	47	37	31	51
PCB #194	77	79	64	63	25	86	65	55	41	70
PCB #208	61	66	57	52	22	75	58	46	39	68
PCB #209	57	71	57	33	15	47	34	29	22	40

Table S 44 Overview of yearly average atmospheric deposition of individual PCB congeners expressed as a daily depostition load (ng/m^2)

Compound	Essen-Vogelheim	Duisburg-Buchholz	Dortmund-Mitte	Duisburg-Wanheim Trafostation	Duisburg-Wanheim Kläranlage	Duisburg-Wanheim KGA Feierabend	Duisburg-Wanheim KGA Biegerhof	Eifel Eifel	Avg.
atmospheric deposition expressed in ng/m^2									
PCB #28	0.51	0.62	0.66	0.24	0.57	0.23	0.22	0.13	0.40
PCB #52	0.89	1.46	0.90	0.57	0.70	0.51	1.03	0.38	0.80
PCB #101	3.6	5.6	4.5	3.6	2.8	3.5	5.2	2.9	4.0
PCB #153	4.4	5.5	5.6	5.3	4.2	4.5	7.4	3.9	5.1
PCB #138	5.0	6.5	6.2	5.9	4.6	5.1	8.4	4.4	5.8
PCB #180	3.1	3.5	3.0	3.5	2.4	2.6	5.2	2.1	3.2

Calculation for the approximation of the lower limit of wipe sample areas

$$\frac{m}{A}(WS)_{Diamon\,\det al.2000} \approx \frac{m}{A}(TSPD)_{LANUV,2014}$$

Literature data of wiped total masses compared to the average total suspended atmospheric deposition (TSPD) from NRW show similar mass loads to a daily deposition load. From the simple equalizing of the congener specific LOQ and the average yearly PCB congener specific concentration in atmospheric depositions the approximation of sampling areas can be performed.

$$LOQ(PCB\#153) = \frac{m}{A}(PCB\#138)_{TSPD}$$

$$\frac{15ng}{A(Sample)} = \frac{5.8ng}{m^2} \qquad A(Sample) = 2.6m^2 \qquad A(Sample) = \frac{15ng}{5.8ng} * m^2$$

Table S 45 LODs for the individual PCB and PCDD/PCDF congeners and homologues

	LOD (the limit of detection)	LOQ (the limit of detection)
PCB homologues	**(ng/Sample)**	**(ng/Sample)**
TriPCBs	1.9	4.4
TetraPCBs	6.8	14
PentaPCBs	28	58
HexaPCBs	46	96
HeptaPCBs	12	26
OctaPCBs	0.97	1.9
NonaPCBs	0.025	0.064
DecaPCB	0.0069	0.015
PCB congeners	**(ng/Sample)**	**(ng/Sample)**
PCB #28	0.26	0.55
PCB #52	1.2	2.5
PCB #101	6.9	14
PCB #153	7.7	16
PCB #138	7.7	15
PCB #180	2.5	4.9
PCB #81	0.0090	0.020
PCB #77	0.047	0.096
PCB #126	0.0051	0.013
PCB #169	0.013	0.035
PCB #123	0.15	0.34
PCB #118	2.6	5.4
PCB #114	0.020	0.048
PCB #105	0.52	1.0
PCB #167	0.41	0.88
PCB #156	0.66	1.3
PCB #157	0.072	0.16
PCB #189	0.045	0.096
TEQ excl. LOD/LOQ	0.00077	0.0020
TEQ ½ LOD/LOQ	0.00073	0.0017
TEQ incl. LOD/LOQ	0.00073	0.0016
PCDD/PCDF homologues	**(pg/Sample)**	
TCDD	-	
PCDD	-	
HxCDD	-	
HpCDD	25	
OCDD	41	
TCDF	-	
PCDF	-	
HxCDF	0.87	
HpCDF	33	
OCDF	12	
PCDD/PCDF congeners	**(pg/Sample)**	
2,3,7,8-TCDD	-	
1,2,3,7,8-PeCDD	-	
1,2,3,4,7,8-HxCDD	-	
1,2,3,6,7,8-HxCDD	-	
1,2,3,7,8,9-HxCDD	-	
1,2,3,4,6,7,8-HpCDD	12	
2,3,7,8-TCDF	-	
1,2,3,7,8-PeCDF	-	
2,3,4,7,8-PeCDF	-	
1,2,3,4,7,8-HxCDF	-	
1,2,3,6,7,8-HxCDF	-	
1,2,3,7,8,9-HxCDF	-	
2,3,4,6,7,8-HxCDF	-	
1,2,3,4,6,7,8-HpCDF	5.7	
1,2,3,4,7,8,9-HpCDF	0.75	
TEQ excl. LOD	-	
TEQ ½ LOD	-	
TEQ incl. LOD	-	

Table S 46 Overview of PCB congener and homologue specific concentrations analysed in wipe samples. Congener and homologue concentrations are given in µg/m^2. Toxicity equivalents (TEQs) are given in ng/m^2. UO = used oil; MR = metal recycling

	UO1	UO2	UO3	UO4	UO5	UO6	MR1	MR2
Sampling area	**0.30**	**0.14**	**0.22**	**0.23**	**0.24**	**0.11**	**0.77**	**0.56**
Sampling site	**staff room**	**working area**	**staff room**	**staff room**	**staff room**	**staff room**	**staff room**	**staff room**
TriPCBs	<LOQ	0.058	<LOQ	0.24	0.021	0.42	0.065	0.035
TetraPCBs	0.072	0.39	<LOQ	0.33	0.083	0.94	0.13	0.23
PentaPCBs	<LOQ	1.9	<LOQ	0.54	<LOQ	1.3	0.096	0.26
HexaPCBs	<LOQ	2.8	<LOQ	0.48	<LOQ	1.9	<LOQ	0.30
HeptaPCBs	0.13	1.9	<LOQ	0.19	<LOQ	0.78	<LOQ	0.098
OctaPCBs	0.015	0.30	<LOQ	0.037	0.0097	0.13	0.0051	0.0097
NonaPCBs	0.00027	0.0069	<LOQ	0.0013	<LOQ	<LOQ	<LOQ	0.00029
DecaPCB	0.00014	0.00050	<LOQ	0.00017	0.00048	0.00052	0.00021	<LOQ
PCB #28	0.0052	0.011	<LOQ	0.017	0.0027	0.050	0.012	0.0046
PCB #52	<LOQ	0.050	<LOQ	0.048	<LOQ	0.066	0.011	0.0089
PCB #101	<LOQ	0.31	<LOQ	0.092	<LOQ	0.24	<LOQ	0.040
PCB #153	<LOQ	0.50	<LOQ	0.086	<LOQ	0.34	<LOQ	0.054
PCB #138	0.062	0.77	<LOQ	0.10	<LOQ	0.43	0.021	0.068
PCB #180	0.037	0.60	<LOQ	0.050	<LOQ	0.22	0.010	0.027
PCB #81	0.00037	0.0050		0.0015	0.00059	0.0022	0.00035	0.00085
PCB #77	0.0011	0.0085		0.0028	0.0016	0.021	0.0017	0.0024
PCB #126	0.00025	0.0012		0.00034	0.000	0.0020	0.000	0.00014
PCB #169	<LOQ	<LOQ		<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
PCB #123	0.0016	0.013	<LOQ	0.0049	0.0021	0.052	0.00081	0.0019
PCB #118	<LOQ	0.27	<LOQ	0.052	<LOQ	0.16	0.013	0.027
PCB #114	0.00032	0.0058	<LOQ	0.0014	0.00031	0.015	0.00048	0.00056
PCB #105	0.0040	0.12	<LOQ	0.019	0.0075	0.13	0.0060	0.010
PCB #167	<LOQ	0.044	<LOQ	0.0043	<LOQ	0.014	0.0013	<LOQ
PCB #156	0.0058	0.12	<LOQ	0.0092	<LOQ	0.032	0.0026	0.0054
PCB #157	0.00077	0.022	<LOQ	0.0021	0.00068	0.019	0.00060	0.00073
PCB #189	0.00037	0.0090	<LOQ	0.0020	<LOQ	0.0053	0.00028	0.00046
TEQ excl. LOQ	0.026	0.14		0.037	0.0099	0.22	0.0069	0.016
TEQ ½ LOQ	0.027	0.14		0.038	0.011	0.22	0.0073	0.017
TEQ incl. LOQ	0.028	0.14		0.039	0.013	0.22	0.0076	0.017

Table S 47 Overview of PCB congener and homologue specific concentrations analysed in wipe samples. Congener and homologue concentrations are given in µg/m^2. Toxicity equivalents (TEQs) are given in ng/m^2. MR = metal recycling; ESR = electronic scrap recycling

	MR3	MR4	MR5	MR6	ESR1	ESR2	ESR3	ESR4
Sampling area	**0.21**	**0.29**	**0.10**	**0.010**	**0.29**	**0.72**	**0.040**	**0.030**
Sampling site	**staff room**	**staff room**	**staff room**	**working area**	**staff room**	**staff room**	**working area**	**working area**
TriPCBs	0.21	0.15	5.7	47	0.78	0.096	20	2.3
TetraPCBs	0.65	0.17	12	209	1.2	0.17	60	3.1
PentaPCBs	2.3	<LOQ	4.3	79	0.71	<LOQ	20	2.3
HexaPCBs	4.2	0.39	2.4	49	0.47	<LOQ	8.6	<LOQ
HeptaPCBs	2.4	0.27	0.95	12	0.21	<LOQ	3.5	<LOQ
OctaPCBs	0.44	0.040	0.12	1.6	0.036	0.0031	0.51	0.19
NonaPCBs	0.012	0.0011	<LOQ	<LOQ	0.0033	<LOQ	0.036	0.0040
DecaPCB	0.011	0.0017	0.0090	0.16	0.0022	0.00014	0.015	0.0037
PCB #28	0.036	0.011	1.5	8.8	0.13	0.014	6.1	0.45
PCB #52	0.11	0.014	0.79	12	0.081	0.012	3.0	0.27
PCB #101	0.50	<LOQ	0.52	12	0.071	<LOQ	2.7	<LOQ
PCB #153	0.83	0.078	0.32	5.1	0.077	<LOQ	1.6	<LOQ
PCB #138	0.96	0.094	0.49	8.7	0.13	<LOQ	2.0	<LOQ
PCB #180	0.75	0.076	0.28	4.2	0.065	<LOQ	1.1	0.24
PCB #81	0.0067	0.00055	0.011	0.24	0.0026	0.00038	0.081	0.0059
PCB #77	0.018	0.0026	0.079	1.9	0.025	0.0029	0.86	0.037
PCB #126	0.0037	0.00034	0.0024	0.024	0.00088	0.000	0.010	0.00083
PCB #169	0.00026	<LOQ	<LOQ	0.011	<LOQ	<LOQ	<LOQ	<LOQ
PCB #123	0.022	0.0023	0.010	0.30	0.0054	0.00075	0.18	0.015
PCB #118	0.24	0.022	0.33	5.0	0.10	0.011	2.1	0.24
PCB #114	0.0047	0.00076	0.0089	0.20	0.0034	0.00041	0.070	0.0084
PCB #105	0.081	0.0091	0.17	2.9	0.070	0.0064	1.3	0.082
PCB #167	0.050	0.0056	0.055	1.3	0.0078	<LOQ	0.10	<LOQ
PCB #156	0.11	0.010	0.046	0.56	0.022	<LOQ	0.23	<LOQ
PCB #157	0.018	0.0015	0.017	0.26	0.0053	0.00034	0.071	<LOQ
PCB #189	0.024	0.0026	0.0087	0.26	0.0022	0.00020	0.027	0.0051
TEQ excl. LOQ	0.40	0.036	0.28	3.3	0.097	0.0082	1.3	0.099
TEQ ½ LOQ	0.40	0.037	0.28	3.3	0.098	0.0086	1.3	0.11
TEQ incl. LOQ	0.40	0.038	0.28	3.3	0.099	0.0089	1.3	0.12

Table S 48 Overview of PCB congener and homologue specific concentrations analysed in wipe samples. Congener and homologue concentrations are given in µg/m^2. Toxicity equivalents (TEQs) are given in ng/m^2. ESR = electronic scrap recycling

	ESR5	ESR6	ESR7	ESR8	ESR9	ESR10	ESR11	ESR12
Sampling area	**0.41**	**0.42**	**0.37**	**0.16**	**0.14**	**0.16**	**0.26**	**0.30**
Sampling site	**staff room**	**staff room**	**staff room**	**staff room**	**staff room**	**staff room**	**staff room**	**staff room**
TriPCBs	0.048	0.080	0.10	0.28	0.94	0.091	0.21	1.8
TetraPCBs	0.11	0.21	0.18	0.61	2.5	0.11	0.93	16
PentaPCBs	0.25	0.18	<LOQ	0.71	2.8	<LOQ	1.1	5.5
HexaPCBs	0.60	<LOQ	<LOQ	<LOQ	1.8	<LOQ	1.5	1.7
HeptaPCBs	0.33	0.10	0.13	<LOQ	0.57	<LOQ	0.53	0.79
OctaPCBs	0.052	<LOQ	0.021	0.018	0.10	<LOQ	0.053	0.099
NonaPCBs	0.0011	0.00075	0.00070	<LOQ	0.0071	<LOQ	0.0014	0.0025
DecaPCB	0.00073	0.00030	0.00055	0.0047	0.0087	0.016	0.0010	0.00075
PCB #28	0.012	0.018	0.023	0.048	0.21	0.010	0.043	0.37
PCB #52	0.010	0.017	0.012	0.054	0.20	<LOQ	0.076	1.2
PCB #101	0.060	0.036	<LOQ	0.11	0.37	<LOQ	0.19	0.81
PCB #153	0.11	0.041	<LOQ	<LOQ	0.32	<LOQ	0.30	0.31
PCB #138	0.14	0.050	0.044	0.12	0.52	<LOQ	0.35	0.40
PCB #180	0.097	0.030	0.042	0.040	0.19	<LOQ	0.14	0.22
PCB #81	0.00057	0.00050	0.00041	0.0019	0.0041	0.00050	0.0040	0.020
PCB #77	0.0018	0.0032	0.0040	0.0077	0.035	0.0028	0.013	0.096
PCB #126	0.00015	0.00017	0.00022	0.00023	0.0017	0.00011	0.00058	0.0013
PCB #169	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
PCB #123	0.0028	0.0019	0.0012	0.0047	0.017	0.0053	0.0083	0.022
PCB #118	0.019	0.016	<LOQ	0.069	0.38	<LOQ	0.14	0.43
PCB #114	0.00033	0.00038	0.00027	0.0024	0.011	0.0051	0.0039	0.022
PCB #105	0.0047	0.0075	0.0053	0.034	0.19	0.011	0.057	0.23
PCB #167	0.0053	0.0021	0.0025	0.0062	0.027	<LOQ	0.015	0.019
PCB #156	0.011	0.0045	0.0060	0.013	0.063	<LOQ	0.031	0.045
PCB #157	0.0014	0.00057	0.0010	0.0041	0.015	0.0061	0.0054	0.0077
PCB #189	0.0027	0.00069	0.0017	0.0016	0.0047	0.0076	0.0024	0.0057
TEQ excl. LOQ	0.017	0.019	0.023	0.029	0.19	0.013	0.068	0.17
TEQ ½ LOQ	0.018	0.020	0.024	0.031	0.20	0.015	0.069	0.17
TEQ incl. LOQ	0.018	0.020	0.024	0.032	0.20	0.017	0.070	0.17

Table S 49 Overview of PCB congener and homologue specific concentrations analysed in wipe samples. Congener and homologue concentrations are given in µg/m^2. Toxicity equivalents (TEQs) are given in ng/m^2. ESR = electronic scrap recycling; TR = transformer recycling

	ESR13	TR1	TR2	TR3	TR4	TR5	TR6	TR7
Sampling area	**0.30**	**0.10**	**0.29**	**0.0090**	**0.020**	**0.034**	**0.020**	**0.14**
Sampling site	**staff room**	**staff room**	**working area**	**working area**	**working area**	**working area**	**working area**	**staff room**
TriPCBs	0.91	0.071	0.064	90	7914	15	2.2	2.8
TetraPCBs	1.5	<LOQ	0.068	213	4595	19	6.3	8.5
PentaPCBs	1.2	<LOQ	<LOQ	156	389	7.8	7.2	9.3
HexaPCBs	1.2	<LOQ	<LOQ	174	163	4.2	4.8	8.2
HeptaPCBs	0.67	<LOQ	0.099	71	60	1.4	<LOQ	3.7
OctaPCBs	0.15	0.020	0.0096	11	7.0	0.21	0.10	0.51
NonaPCBs	0.0056	<LOQ	<LOQ	0.81	0.39	0.0095	<LOQ	0.016
DecaPCB	0.0013	0.0088	0.0027	0.097	0.018	0.00090	0.012	0.0018
PCB #28	0.15	0.012	0.0086	11	999	1.8	0.25	0.57
PCB #52	0.11	<LOQ	<LOQ	14	292	1.1	0.84	0.67
PCB #101	0.20	<LOQ	<LOQ	24	48	0.94	1.3	1.3
PCB #153	0.20	<LOQ	<LOQ	26	24	0.57	<LOQ	1.4
PCB #138	0.27	<LOQ	<LOQ	31	29	0.70	0.99	2.1
PCB #180	0.20	<LOQ	0.028	18	15	0.38	0.33	1.2
PCB #81	0.0048	0.00024	0.00031	0.45	2.5	0.026	0.021	0.030
PCB #77	0.028	0.0022	0.0013	2.9	36	0.21	0.070	0.13
PCB #126	0.0011	0.00024	0.00015	0.28	0.19	0.0030	0.0049	0.0070
PCB #169	<LOQ	<LOQ	<LOQ	0.013	0.0083	<LOQ	<LOQ	0.00034
PCB #123	0.0075	0.0037	0.0012	0.97	1.7	0.029	0.056	0.067
PCB #118	0.15	<LOQ	<LOQ	15	37	0.79	0.59	1.2
PCB #114	0.0039	0.0080	0.00099	0.60	1.8	0.027	0.022	0.036
PCB #105	0.083	0.010	0.0043	7.4	24	0.43	0.23	0.63
PCB #167	0.014	<LOQ	<LOQ	1.7	1.5	0.039	0.052	0.12
PCB #156	0.038	<LOQ	<LOQ	4.0	3.4	0.096	0.095	0.28
PCB #157	0.0073	0.0039	0.0016	0.68	0.69	0.021	0.029	0.059
PCB #189	0.0066	0.0039	0.00092	0.55	0.41	0.011	0.0096	0.035
TEQ excl. LOQ	0.12	0.025	0.015	29	26	0.37	0.53	0.80
TEQ ½ LOQ	0.12	0.028	0.016	29	26	0.38	0.55	0.80
TEQ incl. LOQ	0.12	0.031	0.017	29	26	0.39	0.56	0.80

Table S 50 Overview of PCB congener and homologue specific concentrations analysed in wipe samples. Congener and homologue concentrations are given in µg/m^2. Toxicity equivalents (TEQs) are given in ng/m^2. TR = transformer recycling; TDHW = temporary deposit of hazardous waste

	TR8	TR9	TR10	TR11	TDHW1	TDHW2	TDHW3	TDHW4
Sampling area	**0.44**	**0.030**	**0.030**	**0.21**	**0.24**	**0.020**	**0.020**	**0.96**
Sampling site	**staff room**	**working area**	**working area**	**staff room**	**staff room**	**working area**	**working area**	**staff room**
TriPCBs	9.0	24	<LOQ	0.030	0.049	0.56	22	1.8
TetraPCBs	15	91	3.4	0.22	<LOQ	3.3	66	3.5
PentaPCBs	20	206	19	<LOQ	<LOQ	3.2	68	2.7
HexaPCBs	27	275	16	<LOQ	<LOQ	<LOQ	95	1.2
HeptaPCBs	14	115	6.9	0.17	<LOQ	2.3	52	0.058
OctaPCBs	2.7	17	1.0	0.054	<LOQ	0.35	5.8	0.032
NonaPCBs	0.13	0.60	<LOQ	0.0023	<LOQ	0.012	0.13	0.0022
DecaPCB	0.0042	0.024	0.013	0.00055	0.00011	0.0044	0.12	0.00014
PCB #28	1.5	4.9	<LOQ	0.0085	0.0069	0.11	3.1	0.29
PCB #52	1.2	9.5	0.61	0.018	<LOQ	<LOQ	4.3	0.29
PCB #101	3.2	36	2.4	<LOQ	<LOQ	<LOQ	13	0.41
PCB #153	4.8	53	2.8	<LOQ	<LOQ	<LOQ	17	0.16
PCB #138	6.5	67	3.4	<LOQ	<LOQ	1.0	21	0.23
PCB #180	4.5	34	2.0	0.058	<LOQ	0.70	14	0.059
PCB #81	0.058	0.57	0.031	0.00053	0.000	0.010	0.17	0.0087
PCB #77	0.20	1.4	0.046	0.0017	0.00042	0.088	1.2	0.028
PCB #126	0.029	0.31	0.0033	0.00021	<LOQ	0.0038	0.020	0.00081
PCB #169	0.0028	0.020	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
PCB #123	0.15	1.6	0.18	0.0028	<LOQ	0.024	0.69	0.013
PCB #118	2.6	31	1.4	<LOQ	<LOQ	0.45	8.4	0.23
PCB #114	0.062	0.82	0.10	0.0015	<LOQ	0.014	0.23	0.0061
PCB #105	1.2	12	0.42	0.0061	<LOQ	0.24	3.3	0.10
PCB #167	0.29	2.8	0.30	<LOQ	<LOQ	0.051	1.1	0.012
PCB #156	0.71	6.0	0.34	0.0080	<LOQ	0.13	2.0	0.023
PCB #157	0.12	1.1	0.026	0.0011	<LOQ	0.026	0.38	0.0068
PCB #189	0.15	0.79	0.036	0.0027	<LOQ	0.019	0.27	0.0012
TEQ excl. LOQ	3.2	34	0.43	0.022	0.00007	0.42	2.6	0.098
TEQ ½ LOQ	3.2	34	0.44	0.024	0.0028	0.44	2.7	0.099
TEQ incl. LOQ	3.2	34	0.44	0.025	0.0056	0.45	2.7	0.099

Table S 51 Overview of PCB congener and homologue specific concentrations analysed in wipe samples. Congener and homologue concentrations are given in µg/m^2. Toxicity equivalents (TEQs) are given in ng/m^2. TDHW = temporary deposit of hazardous waste; HWIP = hazardous waste incineration plant

	THDW5	THDW6	THDW7	THDW8	THDW9	THDW10	HWIP1	HWIP2
Sampling area	**0.45**	**0.040**	**0.020**	**0.30**	**0.020**	**0.020**	**0.24**	**0.32**
Sampling site	**staff room**	**working area**	**working area**	**staff room**	**working area**	**working area**	**staff room**	**staff room**
TriPCBs	3.1	0.82	0.74	0.17	32	22	0.070	0.043
TetraPCBs	4.5	3.5	1.0	0.49	51	29	0.17	0.099
PentaPCBs	3.3	7.1	3.0	0.30	11	7.0	<LOQ	<LOQ
HexaPCBs	3.0	7.8	<LOQ	<LOQ	6.6	5.5	0.43	<LOQ
HeptaPCBs	0.86	4.5	<LOQ	0.16	2.5	2.6	0.30	0.25
OctaPCBs	0.14	0.63	0.11	0.025	0.39	0.43	0.062	0.070
NonaPCBs	0.0086	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.0025	0.0030
DecaPCB	0.00080	0.11	0.042	0.0023	0.034	0.073	0.00021	0.00062
PCB #28	0.52	0.14	0.045	0.035	6.8	4.7	0.010	0.0066
PCB #52	0.21	0.22	0.19	0.020	3.1	1.7	<LOQ	<LOQ
PCB #101	0.33	0.91	0.75	<LOQ	1.7	1.2	<LOQ	<LOQ
PCB #153	0.43	1.2	<LOQ	<LOQ	1.2	1.0	0.082	0.052
PCB #138	0.76	1.6	<LOQ	0.068	1.4	1.4	0.098	0.068
PCB #180	0.29	0.94	0.27	0.044	0.71	0.76	0.10	0.089
PCB #81	0.010	0.018	0.0078	0.0018	0.072	0.043	0.00070	0.00039
PCB #77	0.067	0.072	0.018	0.025	0.81	0.48	0.0031	0.0025
PCB #126	0.0043	0.0086	0.0012	0.00045	0.0098	0.0082	0.00020	0.00019
PCB #169	0.00020	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
PCB #123	0.025	0.041	0.022	0.0027	0.095	0.12	0.0025	0.0018
PCB #118	0.46	0.71	<LOQ	0.042	1.2	0.84	0.030	0.019
PCB #114	0.012	0.034	0.023	0.0017	0.045	0.043	0.00057	0.00032
PCB #105	0.29	0.29	<LOQ	0.026	0.63	0.44	0.014	0.0092
PCB #167	0.056	0.071	<LOQ	0.0032	0.075	0.082	<LOQ	<LOQ
PCB #156	0.12	0.14	<LOQ	0.0074	0.15	0.17	0.010	0.0073
PCB #157	0.037	0.034	0.026	0.0015	0.045	0.042	0.0015	0.0013
PCB #189	0.0087	0.048	0.018	0.0011	0.022	0.042	0.0018	0.0017
TEQ excl. LOQ	0.47	0.91	0.12	0.051	1.2	0.93	0.022	0.020
TEQ ½ LOQ	0.47	0.92	0.14	0.052	1.2	0.95	0.024	0.021
TEQ incl. LOQ	0.47	0.93	0.16	0.052	1.2	0.96	0.025	0.022

Table S 52 Overview of PCB congener and homologue specific concentrations analysed in wipe samples. Congener and homologue concentrations are given in µg/m^2. Toxicity equivalents (TEQs) are given in ng/m^2. HWIP = hazardous waste incineration plant; RH= resident houses

	HWIP3	HWIP4	RH1	RH2	RH3	RH4	RH5	RH6
Sampling area	**0.44**	**0.34**	**0.66**	**0.66**	**0.50**	**0.44**	**0.92**	**0.34**
Sampling site	**staff room**	**staff room**	**resident house**	**resident house**	**resident house**	**resident house**	**resident house**	**resident house**
TriPCBs	0.026	0.11	<LOQ	<LOQ	0.011	0.016	0.013	0.018
TetraPCBs	0.045	0.14	<LOQ	<LOQ	0.032	0.040	0.037	0.073
PentaPCBs	0.16	0.23	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
HexaPCBs	0.36	0.48	<LOQ	<LOQ	<LOQ	0.27	<LOQ	<LOQ
HeptaPCBs	0.19	0.34	<LOQ	<LOQ	0.059	0.19	<LOQ	<LOQ
OctaPCBs	0.040	0.092	<LOQ	<LOQ	0.0097	0.025	<LOQ	<LOQ
NonaPCBs	0.0016	0.0044	<LOQ	<LOQ	<LOQ	0.00077	<LOQ	<LOQ
DecaPCB	0.00016	0.00034	0.00012	0.0000	0.0001	0.0001	0.0001	<LOQ
PCB #28	0.0046	0.015	<LOQ	<LOQ	<LOQ	0.0018	0.0020	0.0044
PCB #52	<LOQ	0.013	<LOQ	<LOQ	<LOQ	<LOQ	0.0028	<LOQ
PCB #101	<LOQ	0.044	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
PCB #153	0.069	0.098	<LOQ	<LOQ	<LOQ	0.043	<LOQ	<LOQ
PCB #138	0.092	0.11	<LOQ	<LOQ	<LOQ	0.070	<LOQ	<LOQ
PCB #180	0.063	0.12	<LOQ	<LOQ	0.018	0.058	<LOQ	<LOQ
PCB #81	0.00045	0.00068	0.000	0.000	0.00014	0.00019	0.00015	0.00029
PCB #77	0.0022	0.0039	<LOQ	<LOQ	0.00024	0.00044	0.00044	0.00090
PCB #126	0.00026	0.00046	<LOQ	<LOQ	0.000	0.00020	0.000	0.000
PCB #169	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
PCB #123	0.0016	0.0026	<LOQ	<LOQ	<LOQ	0.0013	0.00045	<LOQ
PCB #118	0.026	0.029	<LOQ	<LOQ	<LOQ	<LOQ	0.0082	0.018
PCB #114	0.00058	0.00070	0.00032	0.00017	<LOQ	0.00015	0.00013	0.00030
PCB #105	0.0087	0.011	<LOQ	<LOQ	<LOQ	0.0033	0.0017	0.0034
PCB #167	0.0040	0.0047	<LOQ	<LOQ	<LOQ	0.0035	<LOQ	<LOQ
PCB #156	0.0093	0.012	<LOQ	<LOQ	0.0028	0.010	<LOQ	<LOQ
PCB #157	0.0014	0.0020	<LOQ	<LOQ	0.00038	0.0013	<LOQ	<LOQ
PCB #189	0.0016	0.0034	0.00019	<LOQ	0.00077	0.0020	<LOQ	<LOQ
TEQ excl. LOQ	0.028	0.048	0.00003	0.00002	0.0039	0.021	0.0043	0.0083
TEQ ½ LOQ	0.029	0.049	0.0010	0.0010	0.0045	0.022	0.0046	0.0092
TEQ incl. LOQ	0.029	0.050	0.0020	0.0020	0.0051	0.022	0.0049	0.010

Table S 53 Overview of PCB congener and homologue specific concentrations analysed in wipe samples. Congener and homologue concentrations are given in µg/m^2. Toxicity equivalents (TEQs) are given in ng/m^2. WS = window surfaces

	WS1	WS2	WS3	WS4				
Sampling area	**2.79**	**2.88**	**4.02**	**4.46**				
Sampling site	**window surface**	**window surface**	**window surface**	**window surface**				
TriPCBs	<LOQ	<LOQ	0.0015	0.0013				
TetraPCBs	<LOQ	<LOQ	<LOQ	<LOQ				
PentaPCBs	<LOQ	<LOQ	<LOQ	<LOQ				
HexaPCBs	<LOQ	<LOQ	<LOQ	<LOQ				
HeptaPCBs	<LOQ	<LOQ	<LOQ	<LOQ				
OctaPCBs	<LOQ	<LOQ	<LOQ	<LOQ				
NonaPCBs	<LOQ	<LOQ	<LOQ	<LOQ				
DecaPCB	<LOQ	<LOQ	<LOQ	<LOQ				
PCB #28	0.00025	0.00024	0.00028	0.00025				
PCB #52	<LOQ	<LOQ	<LOQ	<LOQ				
PCB #101	<LOQ	<LOQ	<LOQ	<LOQ				
PCB #153	<LOQ	<LOQ	<LOQ	<LOQ				
PCB #138	<LOQ	<LOQ	<LOQ	<LOQ				
PCB #180	<LOQ	<LOQ	<LOQ	<LOQ				
PCB #81	<LOQ	<LOQ	<LOQ	<LOQ				
PCB #77	0.000035	0.000034	<LOQ	<LOQ				
PCB #126	0.000008	0.000006	<LOQ	<LOQ				
PCB #169	<LOQ	<LOQ	<LOQ	<LOQ				
PCB #123	<LOQ	<LOQ	<LOQ	<LOQ				
PCB #118	<LOQ	<LOQ	<LOQ	<LOQ				
PCB #114	<LOQ	<LOQ	<LOQ	<LOQ				
PCB #105	<LOQ	<LOQ	<LOQ	<LOQ				
PCB #167	<LOQ	<LOQ	<LOQ	<LOQ				
PCB #156	<LOQ	<LOQ	<LOQ	<LOQ				
PCB #157	<LOQ	<LOQ	<LOQ	<LOQ				
PCB #189	<LOQ	<LOQ	<LOQ	<LOQ				
TEQ excl. LOQ	0.00080	0.00060						
TEQ ½ LOQ	0.00090	0.00072						
TEQ incl. LOQ	0.0010	0.00084						

Table S 54 Overview of PCDD/PCDF congener and homologue specific concentrations analysed in wipe samples. Congener and homologue concentrations are given in ng/m^2. Toxicity equivalents (I-TEQ; TEQ) are given in ng/m^2. AF = accidental fire

	AF1	AF2	AF3	AF4	AF5	AF6	AF7	AF8
Sampling area	**0.020**	**0.16**	**0.14**	**0.081**	**0.035**	**0.015**	**0.025**	**0.29**
Sampling site								
TCDD	n.d.	n.d.	0.040	0.053	n.d.	n.d.	n.d.	0.078
PCDD	n.d.	n.d.	0.11	n.d.	n.d.	n.d.	n.d.	0.026
HxCDD	1.1	0.73	0.17	n.d.	n.d.	n.d.	n.d.	n.d.
HpCDD	<LOD	0.44	<LOD	<LOD	1.3	11	<LOD	<LOD
OCDD	<LOD	0.86	<LOD	<LOD	6.5	41	2.2	<LOD
2,3,7,8-TCDD	<0.012	<0.015	<0.0025	<0.0050	<0.058	<0.079	<0.016	0.0013
1,2,3,7,8-PeCDD	<0.019	<0.021	0.0097	<0.013	<0.096	<0.095	<0.019	<0.0013
1,2,3,4,7,8-HxCDD	<0.053	<0.032	<0.0066	0.014	<0.33	<0.24	<0.044	<0.0028
1,2,3,6,7,8-HxCDD	<0.056	<0.016	<0.010	<0.015	<0.23	<0.20	<0.042	<0.0024
1,2,3,7,8,9-HxCDD	<0.054	<0.018	<0.010	<0.0052	<0.29	<0.15	<0.089	<0.0023
1,2,3,4,6,7,8-HpCDD	<LOD	0.21	<LOD	<LOD	0.80	6.3	0.51	<LOD
TCDF	266	149	0.98	0.41	n.d	n.d	n.d	0.17
PCDF	241	175	0.42	0.26	n.d	n.d	n.d	0.086
HxCDF	85	56	0.11	0.15	<LOD	<LOD	<LOD	0.074
HpCDF	21	12	<LOD	<LOD	1.1	<LOD	<LOD	<LOD
OCDF	6.4	3.7	<LOD	0.22	1.0	<LOD	<LOD	<LOD
2,3,7,8-TCDF	33	23	0.099	0.029	<0.071	<0.20	<0.071	0.010
1,2,3,7,8-PeCDF	18	13	0.036	0.012	<0.30	<0.28	<0.044	0.0046
2,3,4,7,8-PeCDF	32	23	0.031	<0.0029	<0.12	<0.17	<0.056	0.0050
1,2,3,4,7,8-HxCDF	22	14	0.011	<0.0083	<0.19	<0.16	<0.058	0.0034
1,2,3,6,7,8-HxCDF	2.6	2.0	0.0047	<0.011	<0.25	<0.20	<0.064	0.0025
1,2,3,7,8,9-HxCDF	0.55	0.36	<0.0027	<0.0079	<0.29	<0.12	<0.050	<0.0013
2,3,4,6,7,8-HxCDF	4.9	3.3	0.027	0.054	<0.13	<0.19	<0.095	0.014
1,2,3,4,6,7,8-HpCDF	7.3	4.6	<LOD	<LOD	0.90	0.50	0.28	0.024
1,2,3,4,7,8,9-HpCDF	2.7	1.4	<LOD	<LOD	0.096	0.12	0.036	0.0064
I-TEQ excl. LOD	23	16	0.037	0.010	0.025	0.11	0.011	0.0073
I-TEQ ½ LOD	25	16	0.47	0.73	0.20	0.49	0.18	0.16
I-TEQ incl. LOD	27	16	0.91	1.5	0.38	0.86	0.35	0.31
TEQ excl. LOD	16	12	0.034	0.010	0.020	0.082	0.0090	0.0062
TEQ ½ LOD	18	12	0.40	0.64	0.21	0.33	0.095	0.13
TEQ incl. LOD	20	12	0.77	1.3	0.39	0.57	0.18	0.25

Table S 55 Overview of PCDD/PCDF congener and homologue specific concentrations analysed in wipe samples. Congener and homologue concentrations are given in ng/m^2. Toxicity equivalents (I-TEQ; TEQ) are given in ng/m^2. AF = accidental fire; RH = resident house

	AF9	AF10	AF11	AF12	AF13	RH1	RH2	RH3
Sampling area	**0.19**	**0.026**	**0.30**	**0.053**	**0.15**	**0.66**	**0.66**	**0.50**
Sampling site								
TCDD	n.d.	4289	n.d.	n.d.	n.d.	0.0023	0.0039	n.d.
PCDD	n.d.	7557	n.d.	n.d.	n.d.	n.d.	0.0063	n.d.
HxCDD	n.d.	5887	n.d.	n.d.	n.d.	0.011	<LOD	0.024
HpCDD	0.18	2757	0.11	<LOD	2.6	<LOD	<LOD	<LOD
OCDD	0.35	793	0.32	<LOD	26	<LOD	<LOD	0.12
2,3,7,8-TCDD	<0.0059	83	<0.0082	<0.018	0.033	<0.00012	0.00026	0.00069
1,2,3,7,8-PeCDD	<0.015	513	<0.025	<0.040	0.076	<0.00041	<0.00058	<0.0021
1,2,3,4,7,8-HxCDD	<0.013	386	<0.022	<0.075	0.092	<0.00016	<0.00050	<0.0019
1,2,3,6,7,8-HxCDD	<0.011	393	<0.030	<0.080	0.11	<0.00022	<0.00051	0.0019
1,2,3,7,8,9-HxCDD	<0.0091	370	<0.026	<0.077	0.10	<0.00023	<0.0015	0.0015
1,2,3,4,6,7,8-HpCDD	0.12	1478	0.055	<LOD	1.2	<LOD	<LOD	<LOD
TCDF	n.d	18830	0.82	n.d	n.d	0.0083	0.00011	n.d
PCDF	n.d	16331	0.78	n.d	n.d	0.0029	<LOD	0.028
HxCDF	<LOD	12567	0.64	<LOD	1.5	0.011	<LOD	0.027
HpCDF	<LOD	4316	0.18	<LOD	3.5	<LOD	<LOD	<LOD
OCDF	0.13	734	0.086	<LOD	1.5	<LOD	<LOD	0.054
2,3,7,8-TCDF	<0.0054	483	0.037	<0.022	<0.029	0.00072	<0.00063	<0.0012
1,2,3,7,8-PeCDF	<0.0078	1718	0.069	<0.024	<0.038	0.00031	0.00021	0.0021
2,3,4,7,8-PeCDF	<0.0041	1147	0.018	<0.028	<0.028	0.00070	<0.00011	0.0039
1,2,3,4,7,8-HxCDF	<0.010	1686	0.031	<0.033	0.059	0.00050	<0.00071	0.0033
1,2,3,6,7,8-HxCDF	<0.0070	1362	0.019	<0.023	<0.068	0.00041	<0.00021	0.0020
1,2,3,7,8,9-HxCDF	<0.0079	123	<0.018	<0.037	<0.11	<0.00027	<0.00011	<0.00082
2,3,4,6,7,8-HxCDF	<0.011	927	0.033	<0.063	0.16	0.0022	0.0014	0.0039
1,2,3,4,6,7,8-HpCDF	0.068	2993	0.10	<LOD	2.0	<LOD	<LOD	<LOD
1,2,3,4,7,8,9-HpCDF	0.014	456	0.023	0.017	0.016	<LOD	<LOD	0.0023
I-TEQ excl. LOD	0.0025	1623	0.027	0.00017	0.082	0.00075	0.00041	0.0042
I-TEQ ½ LOD	0.014	1623	0.042	1.2	0.15	0.0010	0.00088	0.0050
I-TEQ incl. LOD	0.026	1623	0.057	2.3	0.22	0.0013	0.0014	0.0058
TEQ excl. LOD	0.0021	1614	0.022	0.00017	0.063	0.00060	0.00040	0.0033
TEQ ½ LOD	0.017	1614	0.043	0.99	0.15	0.00099	0.0010	0.0046
TEQ incl. LOD	0.032	1614	0.064	2.0	0.23	0.0014	0.0016	0.0059

Table S 56 Overview of PCDD/PCDF congener and homologue specific concentrations analysed in wipe samples. Congener and homologue concentrations are given in ng/m^2. Toxicity equivalents (I-TEQ; TEQ) are given in ng/m^2. RH = resident house; WS = window surface

	RH4	RH5	RH6	WS1	WS2	WS3	WS4
Sampling area	**0.44**	**0.92**	**0.34**	**2.79**	**2.88**	**4.02**	**4.46**
Sampling site				**window surface**	**window surface**	**window surface**	**window surface**
TCDD	0.013	0.0028	0.0043	n.d.	n.d	0.0023	n.d.
PCDD	0.012	0.0050	0.0029	n.d.	n.d.	n.d.	n.d.
HxCDD	0.049	0.016	0.0083	0.011	0.015	0.013	n.d.
HpCDD	0.14	0.077	<LOD	0.013	0.020	0.022	0.022
OCDD	0.22	0.33	<LOD	0.021	0.031	0.031	0.073
2,3,7,8-TCDD	0.00057	<0.00014	<0.00027	<0.00031	<0.00025	<0.00019	<0.00013
1,2,3,7,8-PeCDD	<0.00040	0.00018	<0.00048	<0.00040	<0.00054	<0.00014	<0.00018
1,2,3,4,7,8-HxCDD	<0.00026	0.00017	<0.00042	<0.00074	<0.0014	<0.00035	<0.00029
1,2,3,6,7,8-HxCDD	<0.00025	0.0011	<0.00042	<0.0011	0.00083	<0.00054	<0.00024
1,2,3,7,8,9-HxCDD	<0.00020	<0.00020	<0.00071	<0.00089	0.0011	<0.00044	<0.00027
1,2,3,4,6,7,8-HpCDD	0.052	0.036	<LOD	0.0067	0.011	0.0089	0.015
TCDF	0.093	0.036	0.040	0.013	0.020	0.0076	<LOD
PCDF	0.080	0.026	0.012	0.011	0.014	0.0057	<LOD
HxCDF	0.044	0.021	0.012	0.0073	0.012	0.015	0.0027
HpCDF	<LOD	<LOD	<LOD	<LOD	<LOD	0.031	<LOD
OCDF	0.29	0.019	<LOD	0.0044	0.0068	0.0053	<LOD
2,3,7,8-TCDF	0.0085	0.0017	0.0026	0.00096	0.00087	0.00037	<0.00015
1,2,3,7,8-PeCDF	0.0064	0.0015	0.00060	0.00092	0.0015	0.00043	<0.00011
2,3,4,7,8-PeCDF	0.0091	0.0012	0.0012	0.0011	0.0014	0.00044	<0.000091
1,2,3,4,7,8-HxCDF	0.0066	0.0018	0.0010	0.00064	0.0019	0.00069	<0.00029
1,2,3,6,7,8-HxCDF	0.0044	0.0014	0.00060	0.00099	0.0015	0.0011	<0.00026
1,2,3,7,8,9-HxCDF	<0.00024	0.00091	<0.00048	<0.00048	<0.00048	<0.0014	<0.00037
2,3,4,6,7,8-HxCDF	0.0052	0.0025	0.0029	0.00090	0.0015	0.0020	0.00024
1,2,3,4,6,7,8-HpCDF	0.015	0.012	<LOD	0.0030	0.0046	0.030	<LOD
1,2,3,4,7,8,9-HpCDF	<LOD	<LOD	<LOD	0.00044	0.0013	0.00032	<LOD
I-TEQ excl. LOD	0.0091	0.0026	0.0014	0.0010	0.0018	0.0011	0.00022
I-TEQ ½ LOD	0.0092	0.0026	0.0019	0.0015	0.0021	0.0014	0.00047
I-TEQ incl. LOD	0.0094	0.0027	0.0024	0.0019	0.0025	0.0016	0.00071
TEQ excl. LOD	0.0068	0.0021	0.0011	0.00080	0.0014	0.00097	0.00017
TEQ ½ LOD	0.0070	0.0022	0.0017	0.0013	0.0019	0.0013	0.00045
TEQ incl. LOD	0.0073	0.0023	0.0024	0.0018	0.0024	0.0016	0.00072

5. General conclusion and outlook

In the thesis presented here analytical methods for the determination of PCBs and PCDD/PCDFs in the surface matrices street dust and wipe samples were developed, validated and applied in environmental monitoring or as part of governmental inspection programs. Street dust and wipe samples taken during this work were evaluated based on international regulations and characterized by spatial differences in concentration levels, congener or homologue patterns. During method development sampling effectiveness for both surface matrices was investigated showing that brushing is a valuable sampling method for the monitoring of POPs like PCBs or PCDD/PCDFs in street dust samples. However, limitations were observed for small sample amounts (< 1g/m^2). As an alternative for the sample collection of obviously small sample amounts wiping of an impervious surface was found to be a suitable sampling method that can complement sampling of surface matrices. Thus, in the context of wipe sampling sufficient transfer efficiencies of deposited PCBs and PCDD/PCDFs in surface films of particulate (< 1g/m^2) and oily liquid nature were presented. It could be demonstrated that the proper choice of wetting solvents used for wipe sampling is indispensable since it was shown that especially for oily liquid films significant deviations in transfer efficiencies with respect to the wetting solvent can occur. With those findings earned especially for wipe sampling of POPs the need for standardization of surface sampling material is highlighted. Commercially available pre-packed solvent wetted wipes for the collection of POPs, pesticides or emerging pollutants are desired to overcome the difficulty of comparing wipe sampling area based concentration data based on different sampling wipes and facilitate the application of wipe sampling as a monitoring tool for diverse problems concerning occupational health and safety issues.

Blank value concentrations for the PCB6 congeners appear to be too high and strongly deviating in wipe samples taken from low contaminated impervious surfaces in indoor and outdoor environments. As a consequence of high blank values correspondingly high LODs for the individual PCB6 congeners were determined which consequently challenges the determination in low contaminated surface films. For future research minimization of blank value concentrations during the complex analytical protocol for the PCB6, dl-PCB and/or PCDD/PCDF determination should be aimed for. Here, alternative clean-up mechanisms in miniaturized scale that avoid the use of large volumes of solvents and reagents may be useful.

The use of PLE for the extraction of POPs from environmental samples was investigated. During this work PLE was found to be the method of choice for the extraction of PCBs and PCDD/PCDFs from street dusts using toluene and furthermore showed its potential to be a suitable alternative for the extraction of those pollutants from wipe samples. However, one should note that during this work PLE was exclusively developed for the extraction of PCBs and PCDD/PCDFs from street dust and adapted for the extraction of wipe samples. Therefore, one should continue the study of PLE for PCBs and PCDD/PCDFs from the wipe sample matrix. This may open the possibility to extract the components of interest more selectively by simultaneously extracting less matrix components, which in turn may lead to a minimization of post extraction clean-up and materials that consequently afford lower blank values. In addition new approaches concerning PLE were developed in the last years. These approaches incorporate parts of the post-extraction clean-up or fractionation steps during PLE [Björklund et al., 2006, Subedi and Usenko, 2012] which is quite conceivable to improve the existing PLE method for street dust. This can be regarded as an additional large potential for time- and cost-reduction during the analytical workflow by simultaneously enhancing sample throughput, e.g., in cases of environmental accidents or large inspection programs.

During this thesis concentrations of PCBs, dl-PCBs and PCDD/PCDFs in diverse street dust samples from NRW were studied. On the basis of 21 street dust samples taken from different sampling site categories (rural, urban, industrially influenced urban, industrial) it could be successfully demonstrated that not only dusts from industrial sites must be regarded as significant reservoirs of POPs. The usefulness of street dust as a naturally occurring passive sampler for PCBs and PCDD/PCDFs has been proven. Consequently, there are now considerations to investigate further persistent halogenated organic component classes like polybrominated diphenylethers or polybrominated dibenzo-p-dioxins and dibenzofurans in street dust.

During this study it could not be clearly pointed out that a correlation between sampling site category and concentration exists. A more significant differentiation between sampling site category and concentration can be enabled if a follow-up study at larger scale is initiated. Dusts with origin from industrial sites exhibit POP concentrations that can even be regarded as secondary sources for the dispersion of POPs, causing transfer and redeposition into their neighbourhood in the form of hot spots. Regulation EC 850/2004 sets a threshold value for total PCB concentration of 50 mg/kg for waste materials that can be exceeded for dust samples taken from industrial sites. NRW as an industrial federal state of Germany is affected

by significant amounts of recycling facilities that deal with, e.g., the recycling of transformers. Revision of this international regulation in order to minimize the threshold value for POPs in waste materials or as in this case in industrial dusts enables discharge of hazardous and highly contaminated materials at an earlier stage and impairs the potential for emission into the environment. Bruckmann et al. (2013) suggested during their trend study of PCBs and PCDD/PCDFs concentrations and depositions in ambient air in NRW that large reservoirs of PCBs and PCDD/PCDFs in soils should be regarded as secondary source for the atmosphere and can be seen as responsible for the only slow decrease of individual congeners in the atmosphere. Implications established for soil/air partitioning should be applied as a first approximation too for street dusts and dusts from industrial sites. Due to the differences in the matrix composition of soils and dusts the suitability of this convention is limited and therefore should be complemented by investigations on the dust/air partitioning in outdoor field experiments.

Björklund, E.; Sporring, S.; Wiberg, K.; Haglund, P.; Holst, C.v. New strategies for extraction and clean-up of persistent organic pollutants from food and feed samples using selective pressurized liquid extraction. *Trends Anal. Chem.* 2006, 25, 318–325.

Subedi, B., Usenko, S. Enhanced pressurized liquid extraction technique capable of analyzing polychlorodibenzo-p-dioxins, polychlorodibenzofurans, and polychlorobiphenyls in fish tissue *J. Chromatogr. A* 2012, 1218, 30–37.

Bruckmann, P.; Hiester, E.; Klees, M.; Zetzsch, C. Trends of PCDD/F and PCB concentrations and depositions in ambient air in Northwestern Germany. *Chemosphere* 2013, *93*, 1471-1478.

6. List of publications

Publications in peer-reviewed journals

Klees, M.; Hiester, E.; Bruckmann, P.; Schmidt, T.C. Determination of polychlorinated biphenyls and polychlorinated dibenzo-p-dioxins and dibenzofurans by pressurized liquid extraction and gas chromatography coupled to mass spectrometry in street dust samples. *J. Chromatogr. A* 2013, *1300*, 17-23.

Klees, M.; Hiester, E.; Bruckmann, P.; Molt, K.; Schmidt, T.C. Polychlorinated biphenyls and polychlorinated dibenzo-p-dioxins and dibenzofurans in street dust of North-Rhine Westphalia, Germany. *Sci. Total Environ.* 2015, *511*, 72-81.

Submitted to *Science of the Total Environment* as "Klees, M.; Hiester, E.; Schmidt, T.C. Analysis of polychlorinated biphenyls, polychlorinated dibenzo-p-dioxins and dibenzofurans in particulate and oily films on impervious surfaces."

Poster presentations

PCBs and PCDD/PCDFs in street dust samples – Determination by pressurized liquid extraction and gas chromatography coupled to mass spectrometry. Essen (Germany) ANAKON 2013, 04.03.-07.03.2013.

7. Curriculum Vitae

Der Lebenslauf ist in der Online-Version aus Gründen des Datenschutzes nicht enthalten.

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9. Erklärung

Hiermit versichere ich, dass ich die vorliegende Arbeit mit dem Titel

„Evaluation of polychlorinated biphenyls, polychlorinated dibenzo-p-dioxins and dibenzofurans in street dust and wipe samples"

selbst verfasst und keine außer den angegebenen Hilfsmitteln und Quellen benutzt habe, und dass die Arbeit in dieser oder ähnlicher Form noch bei keiner anderen Universität eingereicht wurde.

Essen, im Mai 2015

Marcel Klees